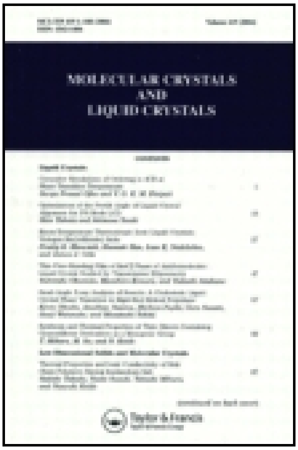

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Synthesis and Photoluminescent Properties of Red Phosphorescent Random Copolymers with Photopatternable Moiety

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*Two types of photopatternable blue emitting random copolymers, poly(VK-ran-CEMA) (**1**) and poly(VK-ran-CEMA-ran-MAE) (**2**), containing UV curable cinnamoyl moieties capable of generating negative type patterned images were synthesized and characterized. In addition, their potential possibility to be used as a photopatternable polymeric host matrix for a red phosphorescent dopant was studied by using UV-Visible absorption and PL emission spectroscopy. The* $\lambda_{max,PL}$ *value of poly(VK-ran-CEMA) (**1**) doped with a red phosphorescent dopant,* $(bsn)_2Ir(acac)$*, was shifted from 343 nm of poly(VK-ran-CEMA) (**1**) to 610 nm, with increasing the content of* $(bsn)_2Ir(acac)$*. Poly(VK-ran-CEMA-ran-*$(bsn)_2IrMAE$*) (**3**), prepared by the reaction of* $[(bsn)_2IrCl]_2$ *with poly(VK-ran-CEMA-ran-MAE) (**2**), exhibited* $\lambda_{max,PL}$ *at 610 nm in the range of red emission. These results implied efficient energy transfer from photopatternable blue emitting random copolymers to a red phosphorescent dopant. It was also found upon UV exposure on the synthesized copolymers that negative patterned images with high resolution were produced by standard photolithographic process.*

Keywords: phosphorescence; photolithographic process; photoluminescence, photopatternable polymer

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INTRODUCTION

Polymer light-emitting diodes (PLEDs) have the advantage of facile processability, high flexibility and thermal stability. Polymers also have lower production costs and can afford uniform films with large flat panel areas due to inexpensive solution processing, such as spin coating process [1–4]. Since one of recent interests in the field of PLEDs has been directed to the realization of full color flat displays, patterned integration of red, green, and blue microstructures with feature sizes less than 100 μm on the same substrate is required for these practical applications. Current trends in the spatial deposition of these materials focus on area-selected electropolymerization [5], photochemical patterning [6], and nonreactive techniques such as screen printing [7], inkjet printing [8] and microcontact printing [9]. Recently, photochemical cross-linking to produce insoluble polymer networks [10] and laser-induced thermal imaging [11] were successfully used in manufacturing devices. Lithographic patterning by photochemical cross-linking of EL polymers has been still considered as a simple and reliable chemical technique, which is compatible with conventional semiconductor photolithography [12–14]. A drawback of PLEDs was their limited quantum efficiency. It has been demonstrated that electrophosphorescent PLEDs are capable of overcoming the limitation. In such PLEDs, a phosphorescent heavy metal complex is doped into a polymeric host material. Energy transfer can be achieved by selectively doping phosphorescent dopant, which is favorable for full color display application.

In this study, PVK-based blue-emitting photopatternable random copolymers functionalized with cinnamoyl groups were synthesized and characterized. By photoinduced cross-linking and insolubilization upon exposure to UV-Visible light, the pattern with high resolution was achieved by dissolution of unexposed regions, resulting in negative patterned images. In addition, their potential possibility to be used as a photopatternable polymeric host matrix for a red phosphorescent dopant was also studied.

EXPERIMENTAL

Materials

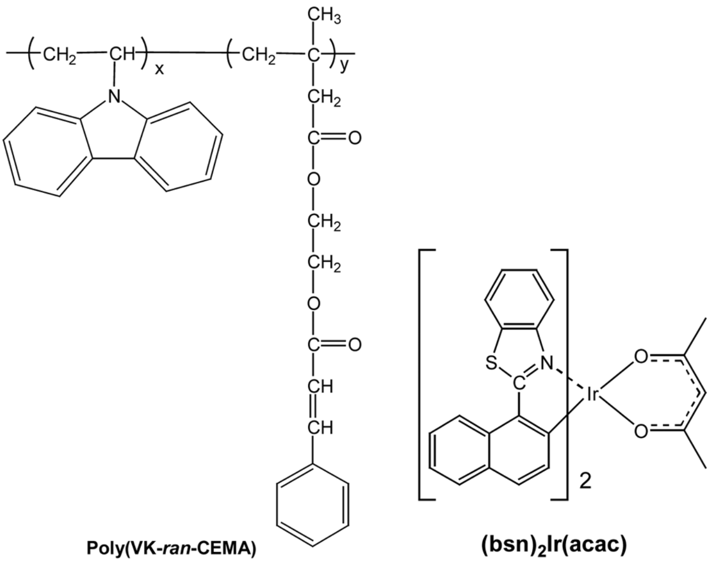
N-Vinyl carbazole (98%), cinnamoyl chloride (98%), 2-(methacryloyloxy)ethyl acetoacetate (MAE, 95%) and hydroxyethyl methacrylate (HEMA, 98%) were purchased from Aldrich Chemical Co. Triethylamine (TEA, 99%) and 2,2-azobisisobutyronitrile (AIBN, 98%) were obtained from Junsei Co. Phosphorescent dopant, $(bsn)_2Ir(acac)$, was synthesized by following the literature previously reported [15]. Solvents such as tetrahydrofuran (THF) and dichloromethane were purified prior to use. All other chemicals were reagent-grades and were used as received.

Synthesis

The structure of photopatternable poly(VK-*ran*-CEMA) (***1***), used as a host matrix for a red phosphorescent dopant , (bsn)$_2$I(acac), is shown in Scheme 1 [16].

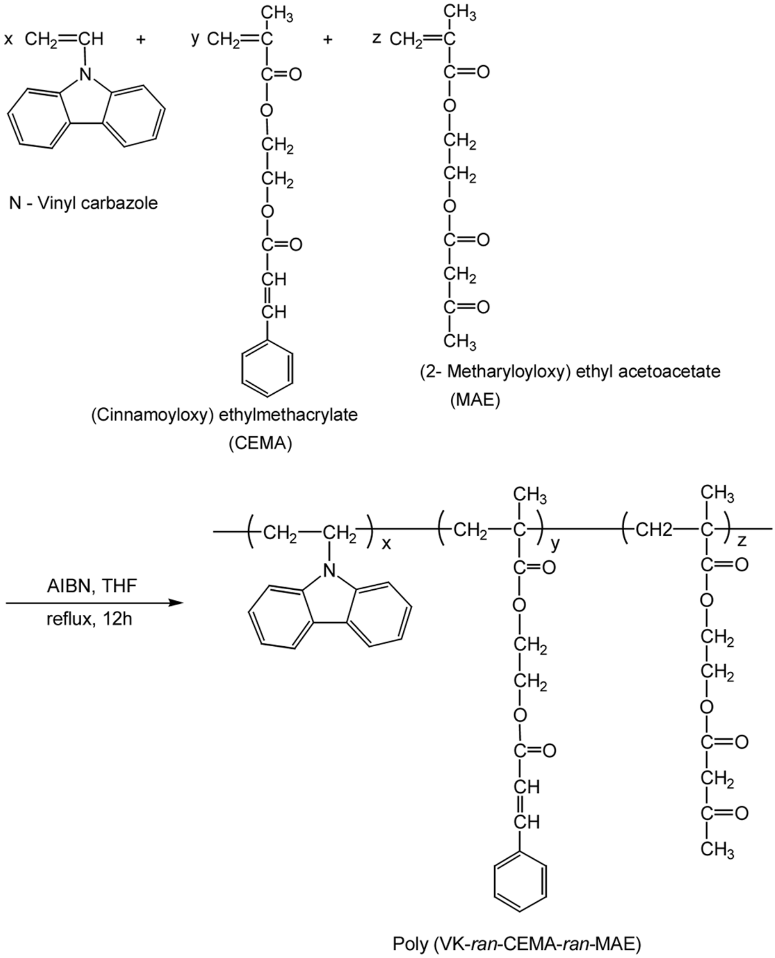
The synthetic route to poly(VK-*ran*-CEMA-*ran*-MAE) (***2***) is presented in Scheme 2.

Cinnamoyl ethyl methacrylate (CEMA). Cinnamoyl chloride (2.468 g, 1.54×10^{-2} mol), HEMA (2.000 g, 1.54×10^{-2} mol) and TEA (1.552 g, 1.54×10^{-2} mol) were dissolved in 40 mL of dichloromethane under nitrogen atmosphere with an ice bath. After removing an ice bath, the reaction was carried out at room temperature for 12 hrs. CEMA (3.00 g, 1.18×10^{-2} mol) was obtained through silicagel column chromatography (*n*-hexane/ethyl acetate = 9/1 v/v). (Yield = 77%). ^{1}H NMR ($CDCl_3$), δ: 7.71 (*d*, 1H, –CH =), 7.54 (*s*, 2H, Ar CH), 7.39



(a) (b)

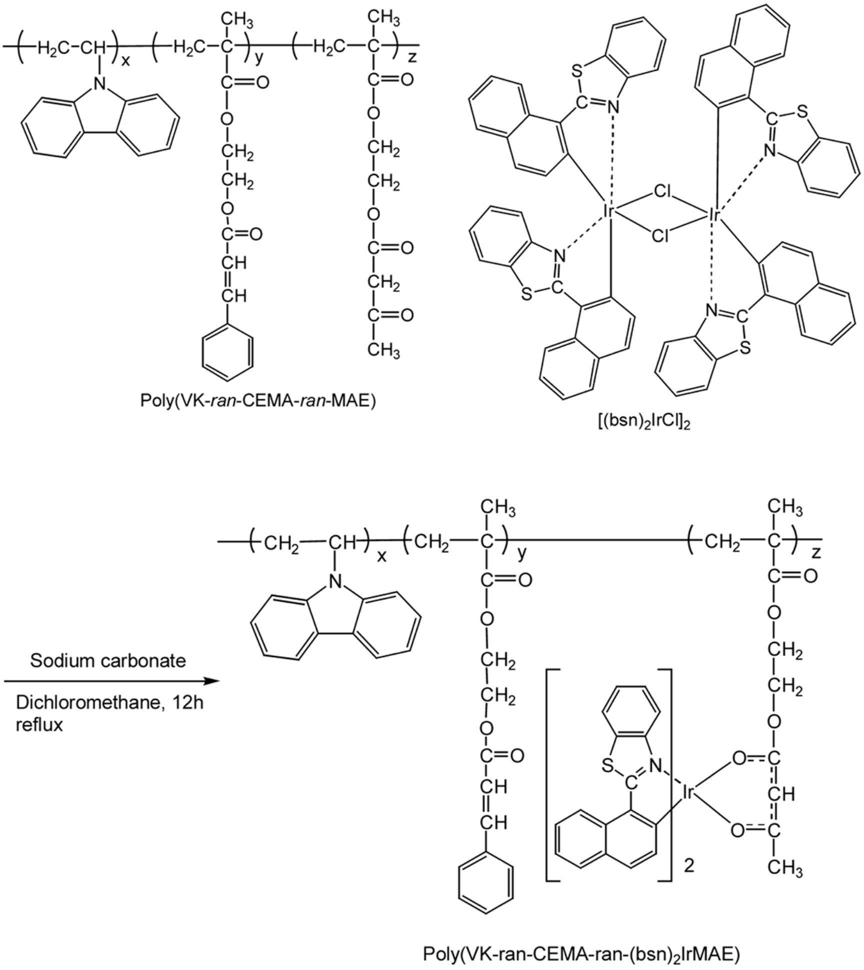
SCHEME 1 Chemical structures of (a) poly(VK-*ran*-CEMA) and (b) (bsn)$_2$Ir(acac).



SCHEME 2 Synthetic route to poly(VK-*ran*-CEMA-*ran*-MAE) (**2**).

(*s*, 3H, Ar CH), 6.46 (*d*, 1H, =CH−Ar), 6.16 (*s*, 1H, −CH−), 5.60 (*s*, 1H, −CH−), 4.46 (*t*, 4H, $-CH_2-CH_2-$), 1.96 (*s*, 3H, $-CH_3$).

*Poly(VK-ran-CEMA-ran-MAE) (**2**).* *N*-Vinyl carbazole (2.00 g, 1.04×10^{-2} mol), CEMA (0.33 g, 0.13×10^{-2} mol) and MAE (0.28 g, 0.13×10^{-2} mol) was dissolved by stirring in 45 mL of THF under nitrogen atmosphere, and then temperature was set to 60°C. At 60°C of reaction temperature, AIBN (0.128 g, 7.80×10^{-4} mol) was added. The polymerization was carried out with stirring for 12 h. The resulting mixture was poured into methanol, filtered, and then dried in vacuum for



SCHEME 3 Synthetic route to poly(VK-*ran*-CEMA-*ran*-(bsn)$_2$IrMAE) (***3***).

12 h at 50°C. Two compositions of poly(VK-*ran*-CEMA-*ran*-MAE) were prepared with the same procedure mentioned above.

Photopatternable poly(VK-*ran*-CEMA-*ran*-(bsn)$_2$IrMAE) (***3***) complexed with red phosphorescent Ir-containing side group was prepared as can be seen in Scheme 3.

Poly(VK-ran-CEMA-ran-(bsn)$_2$IrMAE) (3). [(bsn)$_2$IrCl]$_2$ was synthesized by following the literature previously reported [15]. Poly(VK-*ran*-CEMA-*ran*-MAE) (0.5 g, 0.036 mmol) and [(bsn)$_2$IrCl]$_2$ (0.054 g, 0.036 mmol) and sodium carbonate (2 mg, 0.018 mmole) was added in dichloromethane under nitrogen atmosphere and refluxed for 72 hrs. After reaction, the reaction mixture was cooled down to room temperature and precipitated into methanol. After filtration, washing with methanol several times and vacuum drying, poly(VK-*ran*-CEMA-*ran*-(bsn)$_2$IrMAE) (***3***) was obtained.

Instruments

^{1}H NMR spectra of the synthesized copolymers were measured by using Varian 300 MHz spectroscopy (Mercury 300) using $CDCl_3$ or DMSO-d_6 (Merck Co.) as a solvent. The number- and weight-average molecular weights were measured with a Waters gel permeation chromatography (GPC) system equipped with a 410 differential refractometer, a 510 HPLC pump and a Styragel HR 5E column with THF as an eluent in 1 mL/min of flow rate against polystyrene standards at room temperature. Ultraviolet-visible (UV-Vis) absorption spectra of the copolymers were obtained with Shimadzu UV-2100. The photoluminescence (PL) spectra of the copolymers excited by He-Cd laser at 315 nm were monitored with an optical multichannel analyzer (Laser Photonics, OMA system).

RESULTS AND DISCUSSION

Synthesis and Characterization of Photopatternable Random Copolymers

A series of PVK-based photopatternable random copolymers, poly(VK-*ran*-CEMA) (***1***) and poly(VK-*ran*-CEMA-*ran*-MAE) (***2***), containing cinnamoyl moieties as side chains were prepared. In the case of poly(VK-*ran*-CEMA) (***1***) [16], poly(VK-*ran*-HEMA) was first prepared by radical polymerization of VK and HEMA, and then reacted with cinnamoyl chloride in the presence of TEA for 12 h at room temperature. On the other hand, poly(VK-*ran*-CEMA-*ran*-MAE) (***2***) was prepared by radical polymerization of VK, CEMA and MAE, in which CEMA monomer was synthesized by the reaction of HEMA and cinnamoyl chloride before the polymerization.

Results for molecular weights, polydispersity indices [weight-average molecular weight/number-average molecular weight (M_w/M_n)], and compositions of patternable random copolymers are summarized in Table 1. The number-average molecular weights (M_n's) of random copolymers determined by GPC with THF as an eluent were in the range of 2,800–4,170 g/mol with a polydispersity index of 1.49–2.05. Compositions of poly(VK-*ran*-CEMA) (***1***) were determined from ^{1}H NMR spectra using the integration values of the aromatic hydrogens

TABLE 1 Compositions and Molecular Weights of Patternable Random Copolymers

Polymers	Composition of VK : CEMA : MAE (mole ratio) Monomer	Polymer	GPC M_n	M_w/M_n
Poly(VK-*ran*-CEMA)_1	20 : 80 : 0	14.8 : 85.2 : 0	3,390	1.61
Poly(VK-*ran*-CEMA)_2	40 : 60 : 0	24.5 : 75.5 : 0	4,110	1.70
Poly(VK-*ran*-CEMA)_3	50 : 50 : 0	38.4 : 61.6 : 0	3,030	1.79
Poly(VK-*ran*-CEMA)_4	60 : 40 : 0	49.5 : 50.5 : 0	3,710	2.05
Poly(VK-*ran*-CEMA)_5	80 : 20 : 0	66.3 : 33.7 : 0	2,800	1.49
Poly(VK-*ran*-CEMA-*ran*-MAE)_1	80 : 10 : 10	65 : 15 : 20	4,170	1.85
Poly(VK-*ran*-CEMA-*ran*-MAE)_2	70 : 20 : 10	50 : 20 : 30	3,240	1.74

($\delta = 8.05$–7.12 ppm) of PVK and the methylene peaks ($-O-C\boldsymbol{H}_2-$, $\delta = 3.71$–4.50 ppm) of poly(CEMA). Compositions of poly(VK-*ran*-CEMA-*ran*-MAE) (**2**) were also calculated from ^{1}H NMR spectra (Fig. 1) by comparing the integration values of the aromatic hydrogen's ($\delta = 8.05$–7.12 ppm) of PVK, the methylene peak ($-O-C\boldsymbol{H}_2-$, $\delta = 3.71$–4.50 ppm) of poly(CEMA) and the methylene peak ($-CO-C\boldsymbol{H}_2-CO-$, $\delta = 3.40$–3.71 ppm) of poly(MAE), respectively. It was observed from Table 1 that carbazole content in copolymers

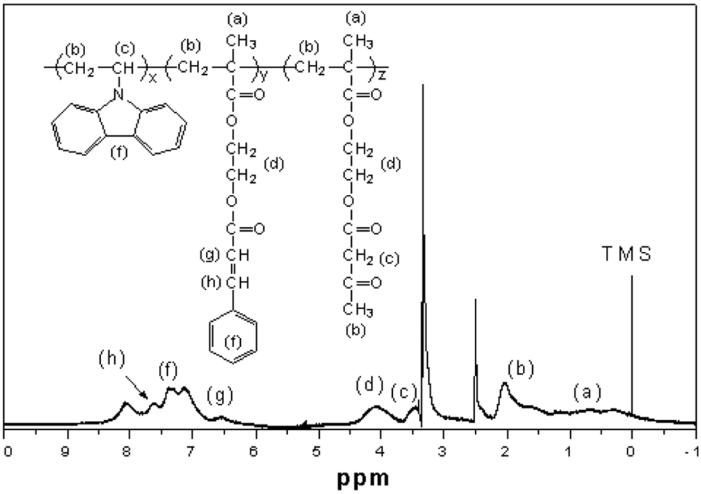


FIGURE 1 ^{1}H NMR spectrum of poly(VK-*ran*-CEMA-*ran*-MAE) (**2**).

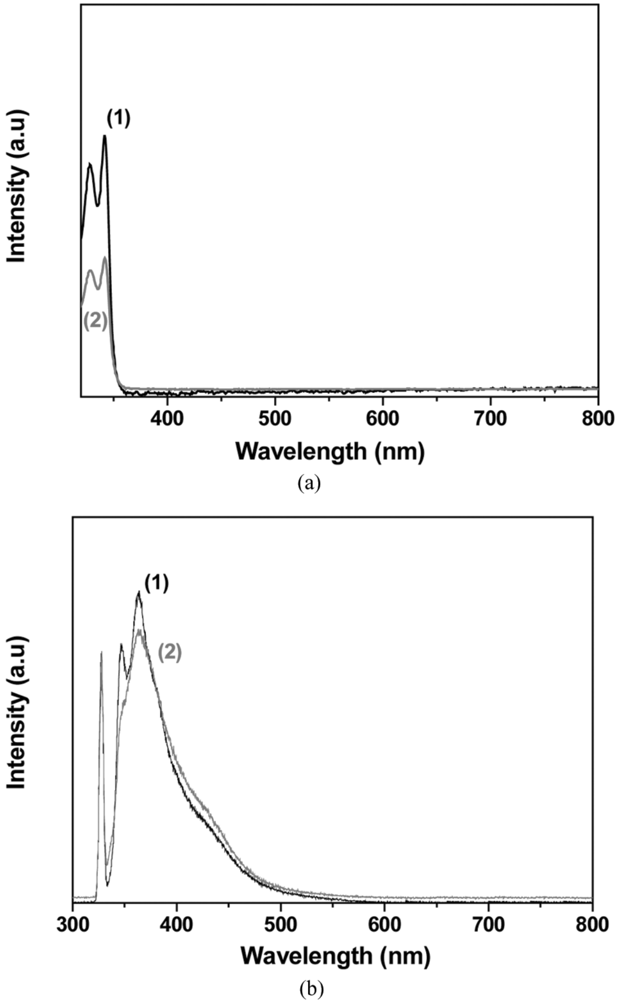
was lower than that in monomer feed. The relatively lower carbazole content in copolymers might be caused by lower reactivity of *N*-vinyl carbazole than that of other methacrylate monomers.

Photoluminescent Properties of Photopatternable Random Copolymers

UV-Visible absorption and PL spectra obtained from the solution of poly(VK-*ran*-CEMA-*ran*-MAE) (**2**) in THF are shown in Figures 2 (a) and (b), respectively. UV-Visible absorption maxima ($\lambda_{max,UV}$) were measured at 343 nm, and PL maxima ($\lambda_{max,PL}$) was found at 370 nm in the range of blue emission, regardless of the compositions of the copolymers. It was good in agreement with previous report [17] that $\lambda_{max,UV}$ of PVK were measured at 330 nm and 344 nm. $\lambda_{max,PL}$ value of PVK was observed at 367 nm, when excited at its own $\lambda_{max,UV}$. As presented from previous study [16], $\lambda_{max,UV}$ and $\lambda_{max,PL}$ of poly(VK-*ran*-CEMA) (**1**) were reported at 343 nm and 370 nm, respectively. Therefore, two types of photopatternable random copolymers ((**1**) and (**2**)) with blue emission in PL spectra could be used as polymeric host matrix for phosphorescent dopants in PLEDs.

UV-Visible absorption and PL emission spectra of poly(VK-*ran*-CEMA) (**1**) doped with a red phosphorescent dopant, $(bsn)_2Ir(acac)$, were measured as a function of the content of dopant, as can be seen in Figure 3 (a) and (b). Poly(VK-*ran*-CEMA)_5 with the highest content of VK, presented in Table 1, was used as the host matrix. As the content of $(bsn)_2Ir(acac)$ dopant was increased in the $(bsn)_2Ir(acac)$/poly(VK-*ran*-CEMA)_5 (**1**) mixture solution, PL intensity of $(bsn)_2Ir(acac)$ dopant at 610 nm steadily increased while PL intensity of poly(VK-*ran*-CEMA)_5 (**1**) decreased, suggesting energy transfer from poly(VK-*ran*-CEMA) (**1**) host matrix to $(bsn)_2Ir(acac)$ dopant.

UV-Visible absorption and PL emission spectra of poly(VK-*ran*-CEMA-*ran*-$(bsn)_2$IrMAE) (**3**) complexed with red phosphorescent Ir-containing side group were also measured, as presented in Figure 4 (a) and (b). Two different compositions of poly(VK-*ran*-CEMA-*ran*-$(bsn)_2$IrMAE) (**3**) were prepared by post reaction of poly(VK-*ran*-CEMA-*ran*-MAE)_1 and poly(VK-*ran*-CEMA-*ran*-MAE)_2 (**2**), respectively, with a red phosphorescent precursor, $[(bsn)_2IrCl]_2$, resulting in the incorporation of a red phosphorescent dopant in the polymer side chain. $\lambda_{max,UV}$ values of two poly(VK-*ran*-CEMA-*ran*-$(bsn)_2$IrMAE) (**3**) were measured at 343 nm, identical to that of



(a)

(b)

FIGURE 2 (a) UV-Visible absorption and (b) PL emission spectra of poly-(VK-*ran*-CEMA-*ran*-MAE) (***2***); (1) poly(VK-*ran*-CEMA-*ran*-MAE)_1 and (2) poly(VK-*ran*-CEMA-*ran*-MAE)_2. (See COLOR PLATE XIV)

poly(VK-*ran*-CEMA-*ran*-MAE) (***2***). However, poly(VK-*ran*-CEMA-*ran*-$(bsn)_2$IrMAE) (***3***) exhibited $\lambda_{max,PL}$ at 610 nm in the range of red emission from the phosphorescent dopant. This also implies efficient energy transfer within poly(VK-*ran*-CEMA-*ran*-$(bsn)_2$IrMAE) (***3***) complexed with red phosphorescent Ir-containing side group.

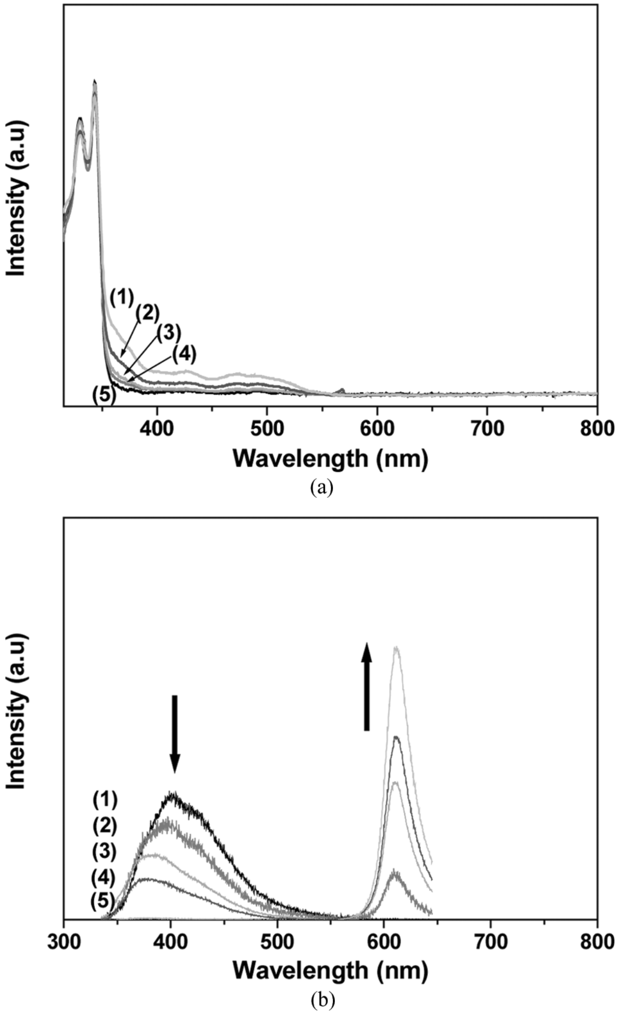
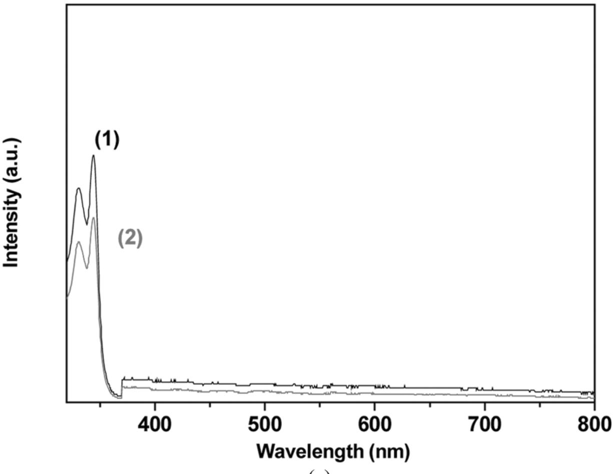


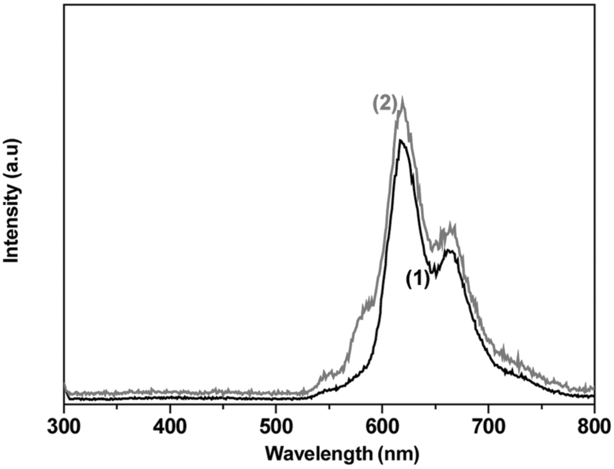
FIGURE 3 (a) UV-Visible absorption and (b) PL emission spectra of (bsn)$_2$Ir(acac)/poly(VK-*ran*-CEMA)_5 (***2***); contents of (bsn)$_2$Ir(acac) (1) 0 wt%, (2) 1 wt%, (3) 3 wt%, (4) 5 wt%, and (5) 10 wt%. (See COLOR PLATE XV)

Formation of Patterns by Photolithographic Process

Solution (1 wt%) of photopatternable random copolymers ((***1***) and (***2***)) was prepared by dissolving in THF. The solution was filtered through a 0.5 μm PTFE membrane filter (Advantec Mfs, Inc.), and then spin-coated with a spin-coating device (SC-300, E. H. Co., Japan) on a



(a)



(b)

FIGURE 4 (a) UV-Visible absorption and (b) PL emission spectra of (1) poly(VK-*ran*-CEMA-*ran*-$(bsn)_2$IrMAE)_1 and (2) poly(VK-*ran*-CEMA-*ran*-$(bsn)_2$IrMAE)_2, prepared from the corresponding poly(VK-*ran*-CEMA-*ran*-MAE)_1 and poly(VK-*ran*-CEMA-*ran*-MAE)_2, respectively. (See COLOR PLATE XVI)

cleaned glass substrate at a series of rotation speeds, 500 rpm for 5 s and then 2500 rpm for 25 s. The resulting film was exposed to UV at 365 nm (intensity of 2,000 mJ/cm^2) through a photomask in a contact mode.

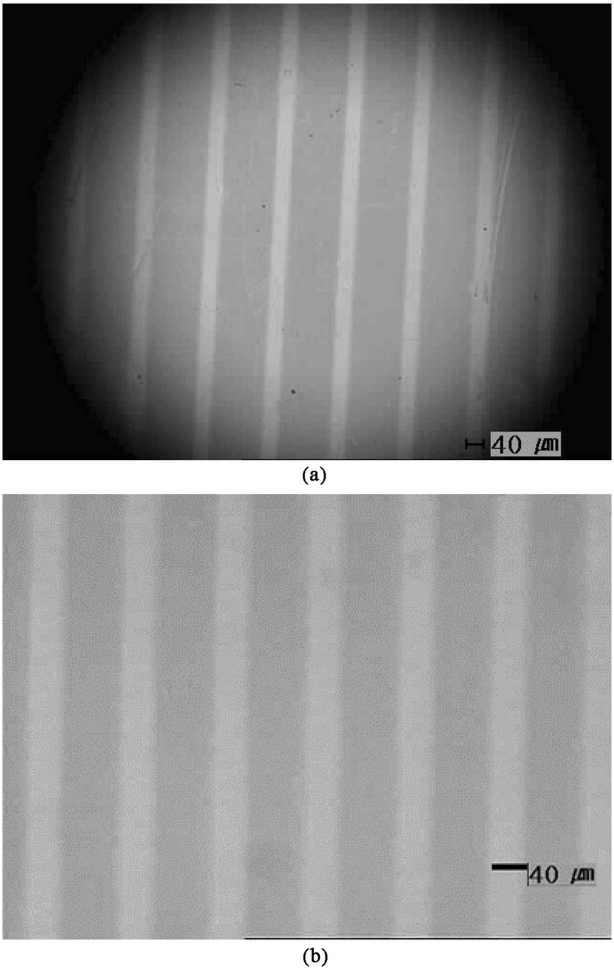


FIGURE 5 Optical microscopic photographs of (a) poly(VK-*ran*-CEMA) and (b) poly(VK-*ran*-CEMA-*ran*-MAE). (line width = 40 μm)

The optical photographs of poly(VK-*ran*-CEMA) (***1***) containing 33.7 mol% of cinnamoyl photosensitive group and poly(VK-*ran*-CEMA-*ran*-MAE) (***2***) were presented in Figure 5 (a) and (b), respectively, as examples of the patterned images formed by conventional lithographic process. Since the UV exposed area became insoluble, the patterned image was obtained upon dissolution of unexposed area with acetone. Therefore, it was found that negative stripe patterns were obtained and the fine lines with 40 μm of width were uniform with smooth surfaces. This observation may provide the possibility that photopatternable random copolymers can be used as blue emitting host matrix materials in conjunction with a photolithographic process.

CONCLUSIONS

We have synthesized and characterized two different types of blue emitting PVK-based random copolymers, poly(VK-*ran*-CEMA) (***1***) and poly(VK-*ran*-CEMA-*ran*-MAE) (***2***), functionalized with photopatternable cinnamoyl groups. From the study on photoluminescent properties, it was found that these copolymers emitted $\lambda_{\max,\mathrm{PL}}$ at 343 nm in the range of blue emission. The $\lambda_{\max,\mathrm{PL}}$ value of poly(VK-*ran*-CEMA) (***1***) doped with a red phosphorescent dopant, $(\mathrm{bsn})_2\mathrm{Ir(acac)}$, was shifted from 343 nm of poly(VK-*ran*-CEMA) (***1***) to 610 nm, with increasing the content of $(\mathrm{bsn})_2\mathrm{Ir(acac)}$. Poly(VK-*ran*-CEMA-*ran*-$(\mathrm{bsn})_2$IrMAE) (***3***), prepared by the reaction of $[(\mathrm{bsn})_2\mathrm{IrCl}]_2$ with poly(VK-*ran*-CEMA-*ran*-MAE) (***2***), exhibited $\lambda_{\max,\mathrm{PL}}$ at 610 nm in the range of red emission. This energy transfer from photopatternable blue emitting random copolymers to a red phosphorescent dopant showed their potential possibility to be used as a photopatternable polymeric host matrix for phosphorescent PLED devices. By photoinduced cross-linking and insolubilization upon UV exposure, the stripe patterns with 40 μm of line width were achieved by developing of unexposed regions, resulting in negative patterned images. The combination of this photolithographic method and the photoluminescent results could offer possibility for full color electrophosphorescence PLEDs.

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