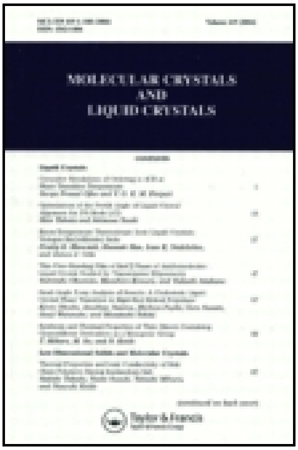

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Electroluminescent Property and Photolithographic Process of Photosensitive Random Copolymers

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Electroluminescent Property and Photolithographic Process of Photosensitive Random Copolymers

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A series of poly(N-vinyl carbazole)-based random copolymers containing photosensitive cinnamoyl moieties capable of generating negative type patterned images were synthesized and characterized. First, poly(N-vinyl carbazole-ran-hydroxyethyl methacrylate) copolymers, P(VK-ran-HEMA), were prepared by free radical polymerization of VK and HEMA monomers using AIBN as an initiator in THF. In second step, cinnamoyl groups were introduced by post reaction. Photoluminescent properties of synthesized photosensitive copolymers were measured and, upon UV exposure, negative patterned images with high resolution were produced by standard photolithographic process.

Keywords: photolithographic process; photoluminescence; photosensitive polymer; PVK

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INTRODUCTION

Polymer light-emitting diodes (PLEDs) have merits of large flat panel fabrication with low production cost by utilizing simple 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. Therefore, much attention has been focused on various methods for full color displays; ink-jet printing [5], screen printing [6], electrochemical dip-pen nanolithography [7], etc. Lithographic patterning of EL polymers has been considered as a simple and reliable chemical technique, which is compatible with conventional semiconductor photolithography [8–10].

In this study, poly(*N*-vinyl carbazole) (PVK)-based copolymers functionalized with photosensitive 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. Since we have recently reported electrophosphorescence of PLEDs with a phosphorescent dopant, $(bsn)_2Ir(acac)$/PVK host systems in terms of luminescence, efficiency, emission color, and energy transfer [11], PVK was selected as a host matrix polymer in this study. The combination of this photolithographic method and the previous results on electrophosphorescence of PLEDs can offer possibility for full color PLEDs.

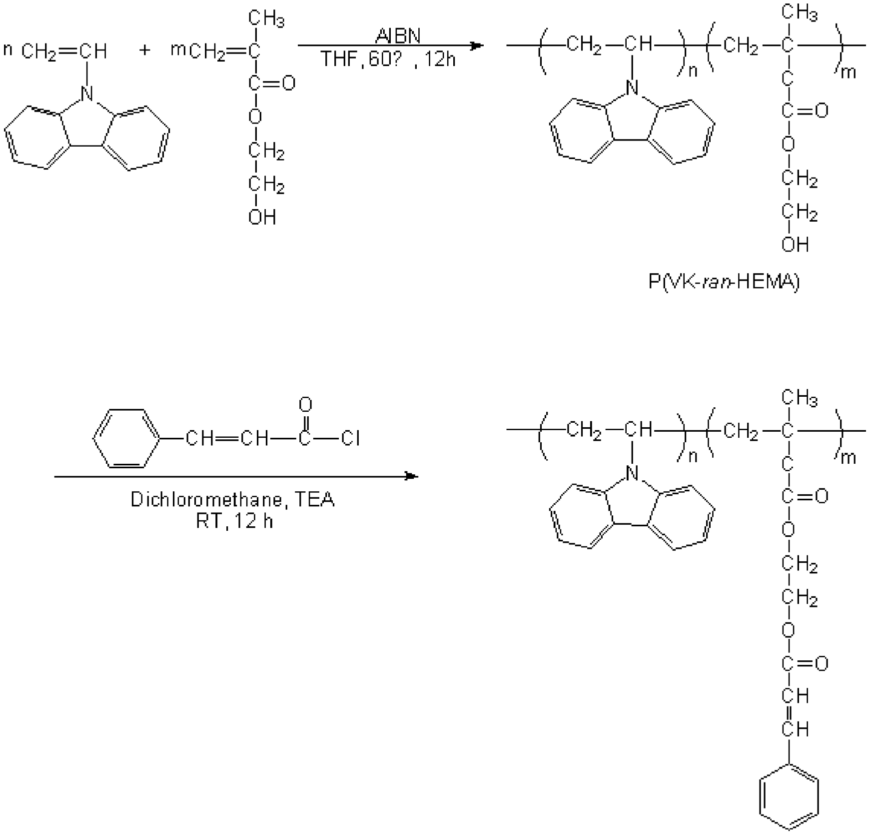
EXPERIMENTAL

Materials

N-Vinyl carbazole (98%), cinnamoyl chloride (98%) 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 [12]. 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 synthetic route to PVK-based photosensitive copolymers (**1**) is shown in Scheme 1.



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SCHEME 1 Synthetic route to photosensitive random copolymer.

Poly(N-vinyl carbazole-ran-hydroxyethyl methacrylate), P(VK-ran-HEMA)

N-Vinyl carbazole (0.483 g, 2.5×10^{-3} mol) and HEMA (0.325 g, 2.5×10^{-3} 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 (0.049 g, 3.0×10^{-4} mol) was added. The polymerization was carried out with stirring for 12 h. The resulting mixture was poured into n-hexane, filtered, and then dried in vacuum for 12 h at 50°C. Five compositions of P(VK-*ran*-HEMA) were prepared with the same procedure mentioned above.

Photosensitive Copolymers (1)

Cinnamoyl chloride (0.065 g, 3.9×10^{-4} mol) was added slowly at 0°C to the solution of TEA (0.038 g, 4.0×10^{-4} mol) and 0.2 g of P(VK-*ran*-HEMA) in 15 mL of dichloromethane. In case of P(VK-*ran*-HEMA) with high content of HEMA, THF was used as solvent due to low solubility of the polymer. The reaction was carried out by stirring at room temperature for 12 h. After reaction, the reaction mixture was filtered and poured into methanol. After filtration and vacuum drying, photosensitive copolymer (**1**) was obtained.

Fabrication of PLED

Doped double layer PLED was made by using the photosensitive copolymer (**1**) as the host of emitting layer. Indium-tin oxide (ITO) coated glass was cut into 2.0 cm × 2.0 cm, and electrode area was prepared by photoetching technique. It was sequentially cleaned in an ultrasonic bath of acetone, methanol, and mixture of isopropyl alcohol and water (1:1 by vol.) solution. A solution (1 wt%) of host polymer:$(bsn)_2Ir(acac)$ (90:10 w:w) in tetrahydrofuran after filtration using MFS filter (0.45 μm pore size) was spin-coated on the ultrasonically cleaned ITO glass at 2500 rpm for 25 s and dried at 80°C for 1 h to give an emissive layer with a thickness of about 250–300 Å. After drying the emission layer the electron transporting Alq_3 layer was deposited with thermal evaporator. Al electrode was deposited at a rate of 20 Å/sec by thermal evaporation to give double layer [ITO/host polymer:$(bsn)_2Ir$-(acac)(90:10 w:w)/Alq_3/Al] PLED.

Instruments

^1H NMR spectra of the synthesized copolymers were measured by using Varian 300 MHz spectroscopy (Mercury 300) using 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 refractomer, 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). Current and luminance vs. voltage profiles were obtained by using a dc power supply connected with Model 8092 A

Digital Multimeter (Hyun Chang Product Co. Ltd) and luminance meter (Minolta LS-100) equipped with close-up lens (No. 110, Φ 40.5 mm) at room temperature, respectively. The photographs of the patterned images were taken with optical microscopy (Olympus BX60, Olympus Optical Co.) connected to a digital camera.

RESULTS AND DISCUSSION

Synthesis and Characterization of Photosensitive Copolymers (1)

A series of PVK-based photosensitive copolymers (**1**) containing cinnamoyl moieties as side chains were prepared, as shown in Scheme 1. In the first step, P(VK-*ran*-HEMA) copolymers were prepared by radical polymerization of VK and HEMA. The results for molecular weights, polydispersity indices [weight-average molecular weight/number-average molecular weight (M_w/M_n)], and compositions of P(VK-*ran*-HEMA) copolymers are summarized in Table 1. The number-average molecular weights (M_n's) of P(VK-*ran*-HEMA) copolymers determined by GPC with THF as an eluent were in the range of 2,800–4,100 g/mol with a polydispersity index of 1.49–2.05. Compositions of P(VK-*ran*-HEMA) copolymers were determined from ^{1}H NMR spectra using the integration values of the aromatic hydrogens ($\delta = 8.05-$ 7.12 ppm) of PVK and the methylene peaks ($-O-CH_2-$, $\delta = 3.83$ ppm) of poly(HEMA). It was observed from Table 1 that carbazole content in copolymers 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 HEMA.

In the second step, photosensitive copolymers (**1**) were synthesized by post reaction of P(VK-*ran*-HEMA) copolymers with cinnamoyl

TABLE 1 Composition and Molecular Weights of Copolymers

	Composition of VK: HEMA (mole ratio)		GPC	
Exp. no.	Monomer feed	P(VK-*ran*-HEMA)^a	Mn	Mw/Mn
P(VK-*ran*-HEMA)_1	20:80	14.8:85.2	3,390	1.61
P(VK-*ran*-HEMA)_2	40:60	24.5:75.5	4,110	1.70
P(VK-*ran*-HEMA)_3	50:50	38.4:61.6	3,030	1.79
P(VK-*ran*-HEMA)_4	60:40	49.5:50.5	3,710	2.05
P(VK-*ran*-HEMA)_5	80:20	66.3:33.7	2,800	1.49

^{a}Calculated from ^{1}H NMR comparing integral ration of aromatic hydrogen peaks of PVK and methylene peaks ($-O-CH_2-$) of poly (HEMA).

chloride in the presence of TEA for 12 h at room temperature. Quantitative cinnamoyl functionalization was indicated by ^1H NMR spectra of the resulting copolymers. Characteristic resonance peak of the hydroxyl proton ($-OH$) at 4.74 ppm was diminished. New characteristic resonance signals such as methine ($-CH{=}CH-$) protons were appeared at 7.61 and 6.53 ppm, respectively. It was also observed that two methylene ($-O-CH_2-CH_2-O$) peaks were combined into one peak, strongly confirming quantitative cinnamoyl functionalization.

Photophysical and Electroluminescent Properties

UV-Visible absorption and PL spectra obtained from the solution of P(VK-*ran*-HEMA) copolymers in THF are shown in Figure 1 (a) and (b). UV-Visible absorption maxima (Fig. 1 (a)) and PL maxima (Fig. 1 (b)) of P(VK-*ran*-HEMA) copolymers were measured at 343 nm and 363 nm, respectively, regardless of the compositions of the copolymers. It was good in agreement with previous report [13] that UV-Visible absorption maxima ($\lambda_{\mathrm{max,UV}}$, π-π^* transition) of PVK were measured at 330 nm and 344 nm. PL maximum ($\lambda_{\mathrm{max,PL}}$) value of PVK was observed at 367 nm, when excited at its own $\lambda_{\mathrm{max,UV}}$.

Figure 2 represents UV-Visible absorption (Fig. 2 (a)) and PL (Fig. 2 (b)) spectra, respectively, of photosensitive copolymers (**1**) with various compositions. Photosensitive copolymers (**1**) exhibited $\lambda_{\mathrm{max,UV}}$ 343 nm, which was the same as the P(VK-*ran*-HEMA) copolymers. PL spectra of photosensitive copolymers (**1**) were slightly broader than those of P(VK-*ran*-HEMA) copolymers, but exhibited $\lambda_{\mathrm{max,PL}}$ at 370 nm in the range of blue-emitting region. The maximum luminance and efficiency of doped [ITO/photosensitive polymer:$(bsn)_2Ir(acac)$ (90:10 w:w)/Alq_3/Al] PLED was measured to be 43 cd/m^2(15 V) and 0.0014 lm/W (15 V), respectively. It appeared that the doped PLED exhibited red emission and showed low color purity due to green emission from Alq_3 layer. Therefore, the thickness of Alq_3 layer in PLED should be further adjusted for the full red emission of $(bsn)_2Ir(acac)$.

Formation of Patterns by Photolithographic Process

A photosensitive polymer solution (1 wt%) was dissolved 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 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.

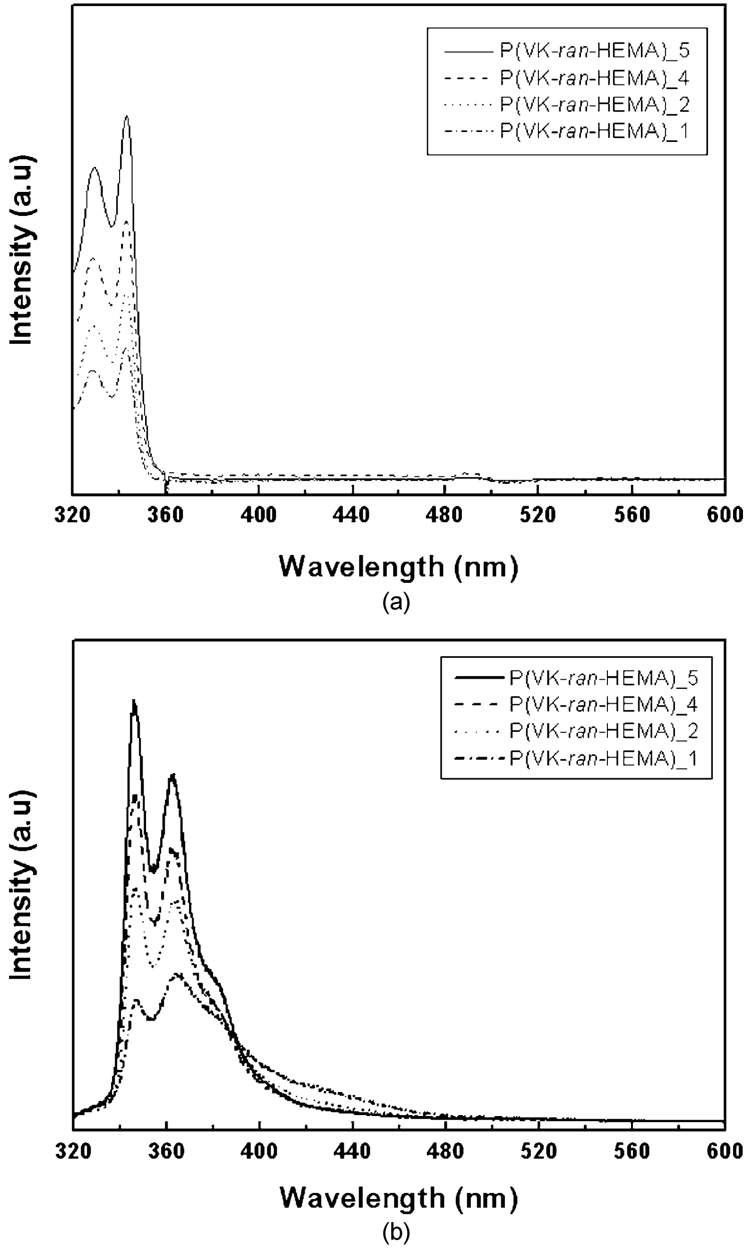


FIGURE 1 (a) UV-Vis absorption and (b) PL spectra of P(VK-*ran*-HEMA) copolymers.

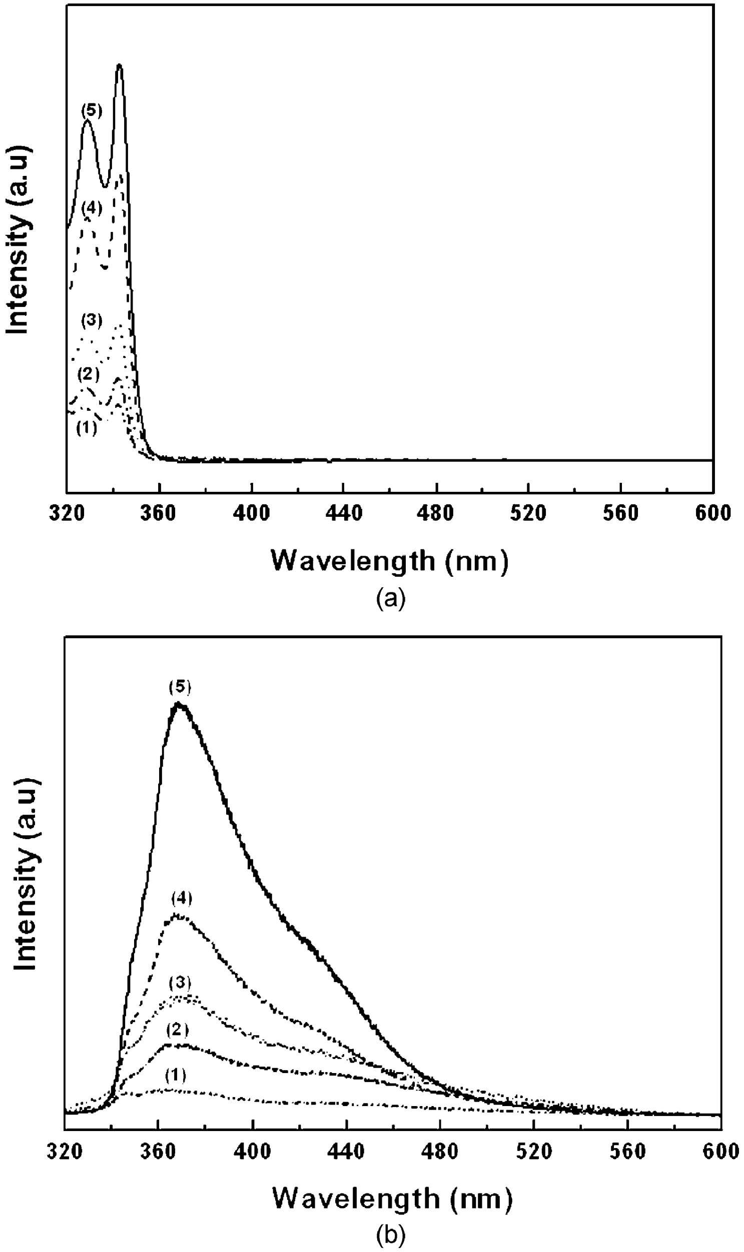
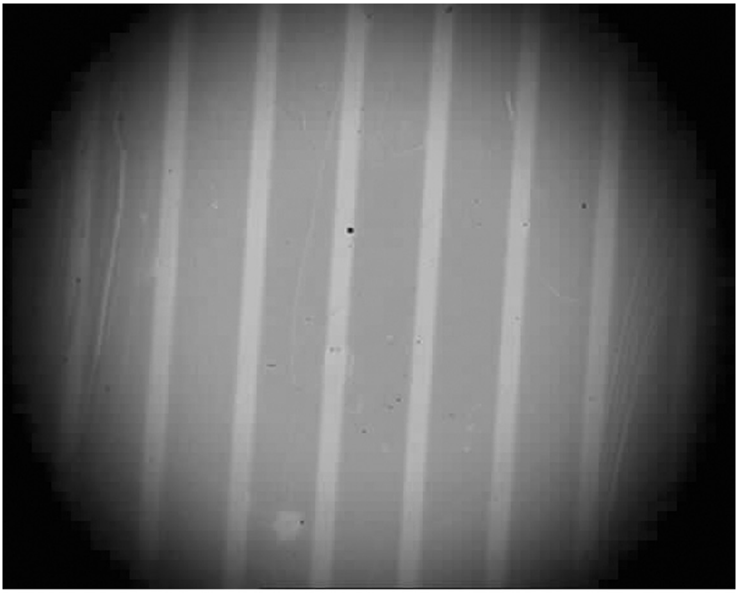
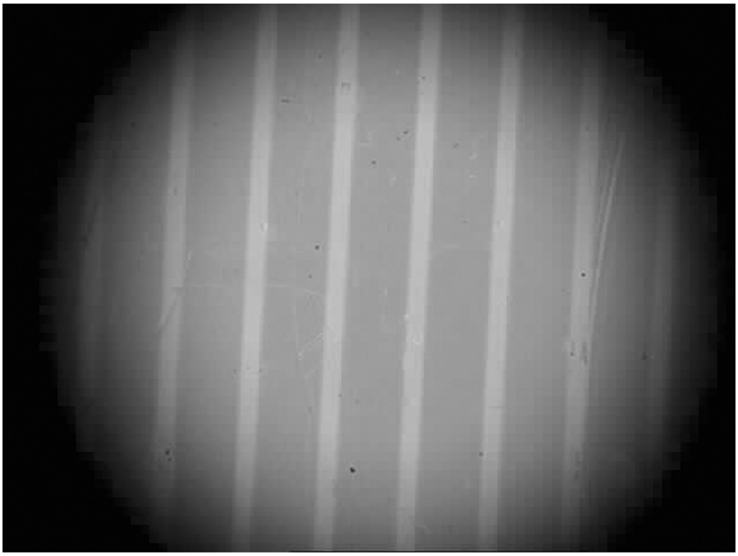


FIGURE 2 (a) UV-Vis absorption and (b) PL spectra of photosensitive copolymers; the content of cinnamoyl groups (1) 85.2 mol%, (2) 75.5 mol%, (3) 61.6 mol%, (4) 50.5 mol%, and (5) 33.7 mol%.



(a)



(b)

FIGURE 3 Optical microscopy photographs of the photosensitive copolymer (**1**) having 33.7 mol% of cinnamoyl group. (line width = 40 μm)

The optical photographs of the photosensitive copolymer (**1**) containing 33.7 mol% of cinnamoyl photosensitive group were presented in Figure 3 as an example 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 photosensitive copolymers (**1**) can be used as blue emitting host matrix materials in conjunction with a photolithographic process.

CONCLUSIONS

We have synthesized and characterized PVK-based copolymers functionalized with photosensitive cinnamoyl groups. In the first synthetic step, poly(*N*-vinyl carbazole-*ran*-hydroxyethyl methacrylate) copolymers, P(VK-*ran*-HEMA), were prepared by free radical polymerization of VK and HEMA monomers using AIBN as an initiator in THF. In second step, cinnamoyl groups were introduced by post reaction. 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.

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