

Articles

Photopatternability of Poly(vinylcarbazole) Bearing Cinnamate Pendants and Its Blends with a Soluble Poly(*p*-phenylene vinylene) Derivative

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Abstract: Poly[(1-(9-carbazolyl)ethylene)-*co*-(3-cinnamoyloxyoctyl-9-carbazolyl)] ethylene (PVK-Cin) was prepared by tethering cinnamate pendants to a carbazole group via an octylene spacer. The photopatternability of the new PVK based-polymer was investigated using a photocrosslinking reaction under UV light illumination ($\lambda = 254$ nm). Blends of the PVK-Cin and a soluble poly(phenylene vinylene) (CzEh-PPV) were employed to study the photocrosslinking behavior. Well resolved lithographic patterns were observed in these polymer systems. PVK-Cin produced a blue light emitting pattern both before and after the photocrosslinking reaction. The blends of PVK-Cin and CzEh-PPV also showed corresponding emissions at 398 and 525 (560) nm in the film state.

Keywords: photopatterning, poly(vinylcarbazole), cinnamate, PPV, carbazole, $2\pi+2\pi$ cycloaddition.

Introduction

Many organic electronic devices developed recently are based on luminescent polymers such as poly(vinylcarbazole) (PVK)¹ and π -conjugated main-chain polymers etc.²⁻⁵ Various kinds of fully conjugated polymers such as poly(phenylene vinylene) (PPV), poly(thienylene vinylene) (PTV), polyfluorene, and their analogues have been intensely investigated in the field of optoelectronic applications.²⁻⁶ Fabrication of micro-circuitry in conventional electronics requires the utilization of photolithography.⁷ Photo-degradation and photocrosslinking reaction can be employed in a photolithographic patterning process. When fabricating the light emitting array devices, we can apply photolithography process using various photoluminescence (PL) polymers. There were a few reports about photopatternable polymer systems so far and their device performance could not be optimized in full under UV light illumination. In order to fulfill the requirements for a photopatterning process, we developed new photoreactive polymer systems containing photocrosslinkable moieties.

In this short report we demonstrate the synthesis and

photocrosslinking⁸ behavior of the photoluminescent PVK derivative (PVK-Cin)⁹⁻¹¹ containing the cinnamate groups in the side chain. We also studied photocrosslinking properties of the blends of PVK-Cin and poly[2-(carbazole-9-yl)-5-(2-ethylhexyloxy)-1,4-phenylenvinylene] (CzEh-PPV) by UV irradiation. The photo- and electroluminescent properties of CzEh-PPV were discussed in our previous report.¹² The possibility for photolithography process is presented using both a new PVK derivative and its blends with CzEh-PPV.

Experimental

Materials. Poly(vinyl carbazole) (PVK, $\overline{M}_n = 124,600$ and $\overline{M}_w = 667,500$), *n*-butyllithium (2.5 M solution in hexane), *trans*-cinnamic acid, and 1,8-dibromooctane were purchased from Aldrich Chem. Co.. AR grade tetrahydrofuran (THF) was purchased from Sam Kyung Chemical Co. and distilled from sodium and benzophenone immediately before use according to literature method.¹³ GR grade dichloromethane was purchased from J. T. Baker Chemical and distilled from CaH prior to use. All reactions were performed under an argon atmosphere unless otherwise stated.

Synthesis of 8-Bromooctyl 3-Phenylacrylate.¹⁴ *Trans*-cinnamic acid (15.0 g, 101 mmol) and potassium carbonate

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(35.0 g, 253 mmol) were mixed in 100 mL of dry dimethylformamide (DMF). At room temperature a solution of 1,8-dibromooctane (27.6 g, 151 mmol) in 20 mL of DMF was added dropwise into the mother solution. The mixture was allowed to reflux for 12 h. After cooling the reaction mixture, it was diluted with 250 mL of dichloromethane and washed with water. The organic layer was dried over MgSO_4 . The solvent was removed *in vacuo* and the residue was purified by silica-gel chromatography (ethyl acetate: hexane 1:10). The product was isolated as yellow oil (27 g, yield 78%).

Synthesis of PVK-Cin. To a solution of PVK (2.00 g, 10.3 mmol) in purified THF (100 mL) was added dropwise at -78°C a solution (10.7 mL, 25.7 mmol) of 2.5 M *n*-butyllithium in hexane over 30 min followed by dropwise addition of a solution of 8-bromooctyl 3-phenylacrylate (6.93 g, 13.3 mmol) in 20 mL of THF. The mixture was slowly warmed up and stirred at room temperature for 12 h.

The reaction mixture was concentrated and diluted in dichloromethane. It was washed with water several times and the organic layer was dried over anhydrous MgSO_4 , and filtered. The filtrate was concentrated under a reduced pressure (ca. 10^{-1} Torr). The crude product was dissolved in THF and the solution was poured into 700 mL of methanol to precipitate the polymer. The crude polymer was purified by reprecipitation. The collected polymer was further purified by a Soxhlet extraction using methanol to remove the low molecular weight oligomers and impurities. The purified polymer was dried *in vacuo* to yield 2.3 g (76%) of PVK-Cin.

Element (CHN) analysis Calc'd. for $(\text{C}_{14}\text{H}_{11}\text{N})_{0.9}(\text{C}_{30}\text{H}_{31}\text{N}_1\text{O}_2)_{0.1}$ (193.09) $_{0.9}$ -(437.24) $_{0.1}$ Calc'd., C: 85.6, H: 5.9, N: 6.8; Found, C: 85.8 H: 5.6, N: 6.9.

Sample Preparation for Photo-Crosslinking. Polymer films (~100 nm thick) were prepared by spin-coating polymer solutions in THF onto quartz substrates. The films were exposed to UV-light ($\lambda_{\text{max}}=256$ nm, Power=16 W) for 3 min. The distance between the light source and surface of a film was 5 cm. When developing the film for making lithographic patterns, we submerged the films in THF for 30 min.

Spectroscopic Measurement. Absorption spectra of polymer films were recorded on a Beckman (CA, U.S.A.) DU-640 spectrometer. The PL spectra were obtained with a Perkin-Elmer (MA, U.S.A.) LS45 luminescence spectrometer.

Results and Discussion

PVK-Cin was synthesized by post-functionalization through lithiation using *n*-butyl lithium followed by reacting with 8-bromooctylacrylate. Ten mole percent of the cinnamate pendants were introduced into the PVK homopolymer. CzEh-PPV was also prepared by following the previous method we reported.¹² The structures of PVK-Cin and CzEh-PPV are shown in Figure 1.

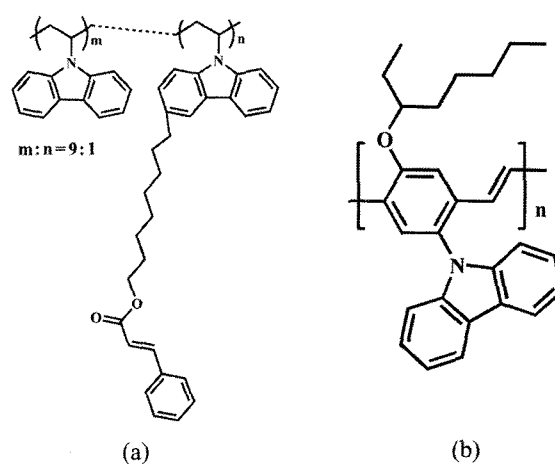


Figure 1. Structures of PVK-Cin (a) and CzEh-PPV (b).

The molecular weights, \overline{M}_n and \overline{M}_w , of PVK-Cin were measured by gel permeation chromatography (GPC; Waters) and determined to be 176,200 and 882,300, respectively with a polydispersity index (PDI) of 2.3. It is believed that the chemical reactions performed on PVK did not induce degradation of the polymer chains as was expected. The glass transition temperature ($T_g=225^\circ\text{C}$) of PVK-Cin is somewhat lower than that of the PVK (250°C) polymer, which is ascribed to the presence of the cinnamate pendant groups with a flexible octylene spacer.

Photocrosslinking Properties of PVK-Cin and Its Blends. Photo-dimerization of cinnamic esters has been the subjects of many studies under UV light illumination and their photocrosslinking mechanisms are relatively well understood.¹⁵ In the present investigation, we observed that PVK-Cin readily undergoes $2\pi+2\pi$ cycloaddition when exposed to the UV light ($\lambda_{\text{max}}=254$ nm) at 150°C . When a 100 nm thick film of PVK-Cin was irradiated for 7 min, no soluble portion could be extracted in THF when subjected to Soxhlet extraction for 24 h, which is an indirect evidence of crosslinking.

Figure 2 displays the absorption behavior of PVK-Cin and its blends with CzEh-PPV. The film samples were utilized for taking the spectra before (A) and after (B) UV irradiation. We could not observe any discernible spectral changes at around 250-270 nm due to photocrosslinking between the double bonds of cinnamate groups. This is attributed to the fact that only a small part of the cinnamate groups might be involved in the photoreaction. Besides the photoproduct between cinnamate groups, the alkylene carbazole units are likely to be involved in crosslinking reactions through the mechanism by which *N*-substituted carbazoles undergo photodimerization.^{16,17}

We, however, found that the spectral feature of CzEh-PPV film is completely different from the former: As can be seen in Figure 2(B), the original strong absorbance at $\lambda_{\text{max}}=463$ nm due to $\pi-\pi^*$ transition was drastically reduced and

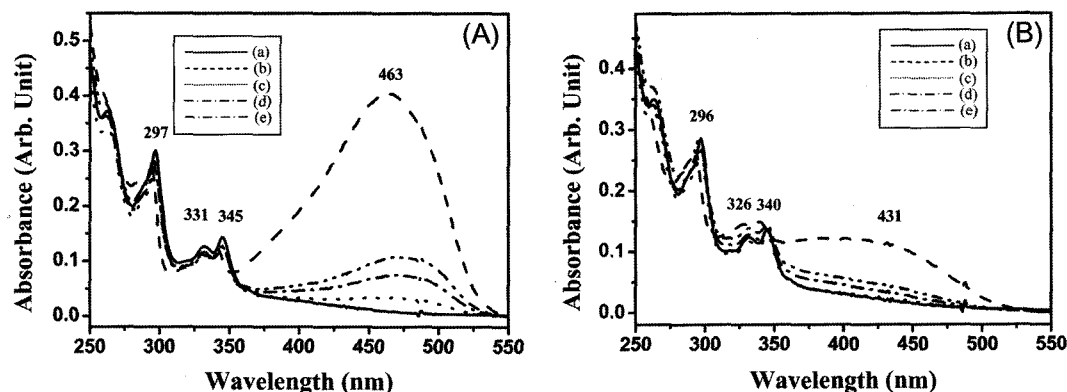


Figure 2. Absorption spectra of PVK-Cin and its blend films: (A) before UV illumination and (B) after UV illumination. (a) PVK-Cin; (b) CzEh-PPV; (c) PVK-Cin/CzEh-PPV (10 wt%); (d) PVK-Cin/CzEh-PPV (30 wt%); (e) PVK-Cin/CzEh-PPV (50 wt%).

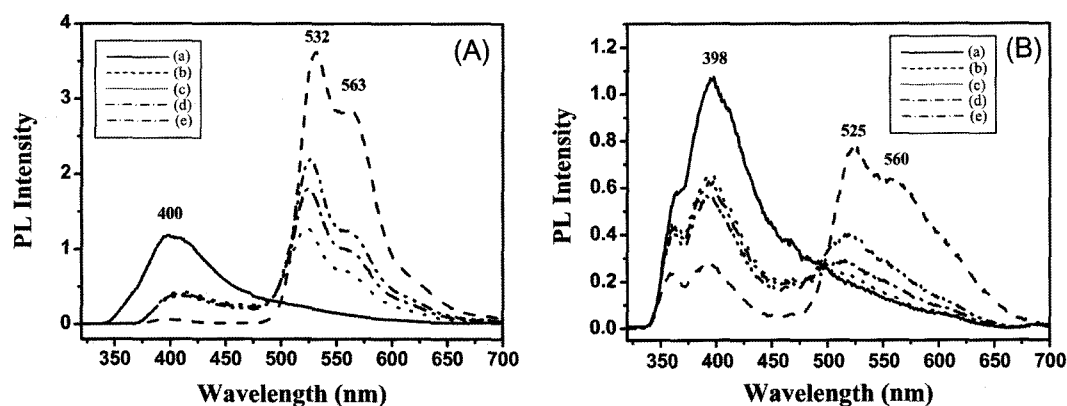


Figure 3. PL spectra of PVK-Cin and its blend films: (A) before UV illumination and (B) after UV illumination. (a) PVK-Cin; (b) CzEh-PPV; (c) PVK-Cin/CzEh-PPV (10 wt%); (d) PVK-Cin/CzEh-PPV (30 wt%); (e) PVK-Cin/CzEh-PPV (50 wt%).

the spectrum was blue-shifted after crosslinking. Figure 3 exhibits photoluminescence spectra of the same polymer samples we used in absorption spectral analysis before (A) and after (B) UV illumination.

In Figure 3(A), we hardly observe a possible emission around 400 nm by the carbazole groups of CzEh-PPV (Curve (b)) before UV irradiation. From this figure, it is clearly evident that the emission spectrum of PVK and absorption spectrum of CzEh-PPV overlap favorably which enables an efficient Förster energy transfer. This is explained by a fast energy transfer process from the carbazole groups to the π -system of the main chain as discussed in our previous report.¹²

After UV illumination, new PL peaks arisen from an isolated carbazole ring appeared at 362 and 394 nm (see Figure 3(B)). This observation manifestly suggests that the double bonds in vinylene groups in the chain are involved in photocrosslinking reactions.

When taking PL spectrum of the mixtures of PVK-Cin and CzEh-PPV, we could observe blue and green emissions, correspondingly (see Figure 3). The blue emission is originated from the PVK polymer backbone before and after crosslink-

ing. The green emission is due to the presence of CzEh-PPV. The higher the concentration of CzEh-PPV is, the stronger the emission intensity at around 525–563 nm becomes.

Moreover, when the mixtures were exposed at 150 °C to UV light for 10 min in the presence of 1 wt% of benzophenone, no soluble portion of polymers were detected after a Soxhlet extraction in THF. We thought that cross-propagation between two polymers might occur to form a photocrosslinked matrix. The miscibility of two polymers was investigated by using DSC. By observing a single T_g at around 176 °C, good miscibility between the two polymers was confirmed (e.g. T_g = 145 °C for CzEh-PPV and 225 °C for PVK-Cin). This observation strongly supports the formation of cross-propagation induced by expected intermolecular interactions and induction of energy transfer process. It can be conjectured that there is a possibility for the partial formation of inter-penetrating network (IPN)¹⁸ structures between the two polymers.

Photo-Patterning Image Analysis under a UV Illumination. Figure 4 shows the micrographs of elaborated patterns obtained from the mixture of PVK-Cin and CzEh-PPV.

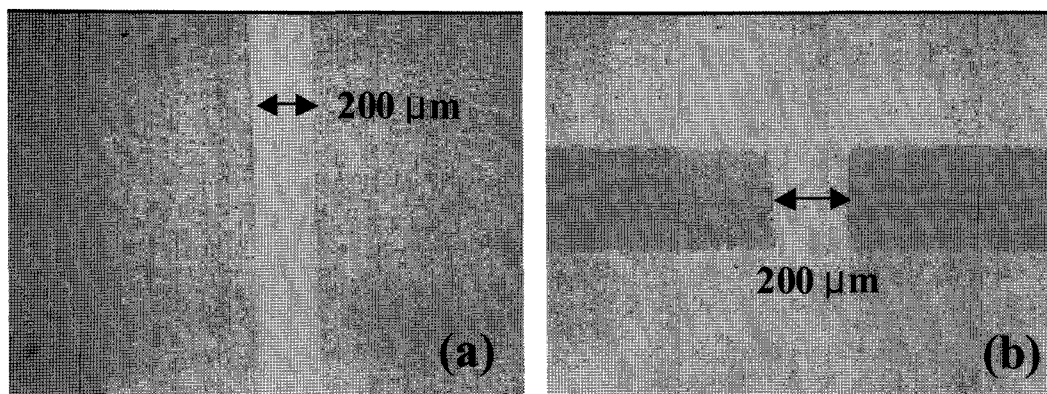


Figure 4. Optical micrographs of the patterned images formed by UV irradiation. (a) PVK-Cin and (b) CzEh-PPV.

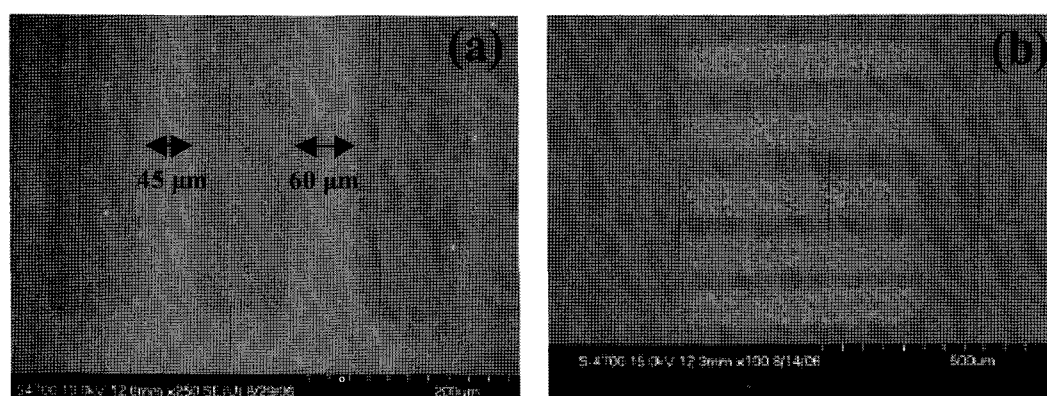


Figure 5. Scanning electron micrographs of the patterned images formed by UV irradiation. (a) PVK-Cin and (b) CzEh-PPV.

After exposing the films to UV light through a photo-mask, we developed them in THF to leave only exposed areas that underwent photocrosslinking reaction. SEM images of the lithographic patterns were also obtained from the blend (see Figure 5). Highly resolved patterns were obtained and thus the polymers were figured out to behave as a negative photoresist. We are presently trying to elucidate the exact crosslinking mechanism of the blend materials.

Conclusions

We successfully synthesized a PVK-based photocrosslinkable polymer containing cinnamate pendants. UV irradiation could induce efficient $2\pi+2\pi$ cycloaddition between the double bonds in cinnamate groups. We utilized two different types of photo-crosslinkable polymer systems in this study; PVK bearing a cinnamate group in the side chain and mixtures of PVK-Cin and CzEh-PPV. We obtained well resolved lithographic patterns using these polymer systems.

The results of this work suggest that electroluminescent polymer patterns can be fabricated by the conventional photolithographic method although luminescence properties of polymers may be deteriorated to some extent after photo-

crosslinking.

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