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Photoreactive hole-transporting polymer bearing oxetane moieties and its application to green polymer light-emitting diodes

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ABSTRACT

A new hole-transporting polymer was prepared by the copolymerization of 9-(4-vinylbenzyl)-9*H*-carbazole and 3-methyl-3-(4-vinyl-benzyloxymethyl)-oxetane in the presence of α, α' -azobisisobutyronitrile (AIBN). The latter contains an oxetane unit that is cationically photopolymerizable. It was characterized by NMR, GPC, IR spectroscopy, TGA, and differential scanning calorimetry (DSC). Multilayer polymer light-emitting diodes (PLEDs) were fabricated layer by layer by using the spin-coating method with an organic solution of a photoreactive copolymer. Organic soluble poly[2-(carbazol-9-yl)-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (CzEh-PPV) that carries hole-transporting carbazole pendants was also synthesized and employed as a green-emitting material in PLEDs. After UV illumination for photoreaction in the new photoreactive oxetane-based copolymer (VCz-Ox), we could spin coat the CzEh-PPV solution for the next layer. The hole-transport capability of the copolymer was evaluated in multilayer PLEDs that were fabricated to test the device performances. © 2008 Elsevier B.V. All rights reserved.

1. Introduction

Recently, semiconducting organic materials have attracted considerable interest as suitable candidate materials in the fields of electronics and optoelectronics [1–3]. Among the many applications of these organic materials, electroluminescent (EL) devices using organic materials with a low molar mass are the most popular and have already been employed in practical applications such as flat-panel or flexible display devices [4–9].

In conventional single-layer EL devices, high-energy barriers for charge injection/transport, low mobility of charge carriers, and a recombination zone close to the cathode lead to decreased efficiencies and lifetimes. Efficient hole carrier transport is a prerequisite for realizing high-performance EL devices accompanied by wellbalanced hole and electron injection. Better characteristics have been achieved by changing the device structure to a multilayer design with specially designated layers for electron and hole transport.

Polymeric EL materials allow for the use of inexpensive solution processing methods for layer fabrication because of their excellent film-forming properties and high film stability. However, the solution deposition method for multilayer polymer light-emitting diodes (PLEDs) has a disadvantage; already coated layers tend to be swollen or dissolved by the solvent that is used to apply the upper layer. A common method used to overcome this shortcoming is to render the applied layer insoluble by crosslinking before the next coating procedure [10–15].

In this study, we selected an oxetane-containing styrene monomer that is copolymerized with carbazole-based holetransport monomers as a photopolymerizable moiety [15–17]. The oxetane moiety is connected to the styrene backbone via a short methyl spacer to guarantee a high glass transition temperature before and after crosslinking. It has already been found that oxetane-containing polymers can undergo fast cationic polymerization in a solid state with high conversion, and the high-quality film can be sustained even after the photocuring process [18,19]. During device processing, a solution of the polymer that is mixed with small amounts of a photosensitive cationic initiator is spin-coated on the substrate and sequentially crosslinked by UV irradiation; this leaves the resulting insoluble film ready for the application of the next layer. We employed a poly(phenylene vinylene) derivative, that is, poly[2-(carbazol-9yl)-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (CzEh-PPV), as an emitting material and investigated the performance of an EL device by utilizing the new hole-transport polymer.

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2. Experimental

2.1. General

All commercially available starting materials were purchased from Aldrich, or ACROS Co. and used without further purification unless otherwise stated. The radical initiator, α , α' -azobisisobutyronitrile (AIBN) was recrystallized in acetone before use. HPLC grade tetrahydrofuran (THF) and toluene were purchased from Samkyung Chemical Co. and distilled from sodium and benzophenone immediately before use. Dimethylformamide (DMF) was also purchased from Fisher and distilled from CaH₂ prior to use. All reactions were performed under an argon atmosphere unless otherwise stated.

2.2. Synthesis

2.2.1. 9-(4-Vinyl-benzyl)-9H-carbazole, 1

Sodium hydride (2.4 g, 55 mmol) was suspended in dried dimethylformamide (DMF, 50 mL) at 0 °C. Carbazole (8.36 g, 50 mmol) in DMF (100 mL) was added dropwise into the mother solution and stirred for 0.5 h. Then, 1-chloromethyl-4-vinyl-benzene (9.15 g, 60 mmol) in DMF (50 mL) was also added dropwise and the reaction mixture was kept stirring at room temperature for 12 h. Finally the reaction mixture was poured to 100 mL of water and then, it was neutralized with aqueous 2 M HCl. After filtering the reaction mixture and concentrating it, the crude product was purified by silica gel column chromatography (EA:chloroform = 1:20) to give a white powder in 74% yield (10.5 g, 37.0 mmol).

¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J*=8.0Hz, 2H), 7.44 (t, *J*=8.0Hz, 2H), 7.37 (d, *J*=8.0Hz, 2H), 7.31 (d, *J*=8.0Hz, 2H), 7.26 (t, *J*=8.0Hz, 2H), 7.11 (d, *J*=8.0Hz, 2H), 6.66 (dd, *J*₁=11.2Hz, *J*₂=17.6Hz, 1H), 5.69 (d, *J*=17.6Hz, 1H), 5.52 (s, 2H), 5.21 (d, *J*=11.2Hz, 1H).

2.2.2. 3-Methyl-3-(4-vinyl-benzyloxymethyl)-oxetane, 2

Sodium hydride (2.4 g, 55 mmol) was suspended in dried dimethylformamide (DMF, 50 mL) at 0 °C. (3-Methyl-oxetan-3-yl)-methanol (5.1 g, 50 mmol) in DMF (100 mL) was added dropwise into the mother solution and stirred for 0.5 h. Then, 1-chloromethyl-4-vinyl-benzene (9.15 g, 60 mmol) in DMF (50 mL) was also added dropwise and the reaction mixture was kept stirring at room temperature for 12 h. Finally the reaction mixture was diluted with 100 mL of diethyl ether and washed twice with 150 mL of water. The organic layer was dried over Na₂SO₄, and the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (EA:chloroform = 1:10) to give a viscous liquid in 70% yield (7.2 g, 33.0 mmol).

¹H NMR (300 MHz, CDCl₃) δ 7.40 (d, *J*=9.0 Hz, 2H), 7.30 (d, *J*=9.0 Hz, 2H), 6.72 (dd, *J*₁=12.0 Hz, *J*₂=16.8 Hz, 1H), 5.76 (d, *J*=16.8 Hz, 1H), 5.24 (d, *J*=12.0 Hz, 1H), 4.56 (s, 2H), 4.52 (d, 2H), 4.36 (d, 2H), 3.51 (s, 2H), 1.33 (s, 3H).

2.2.3. Synthesis of copolymer, 3

1 (2.55 g, 9 mmol) and 2 (0.65 mg, 3 mmol) were dissolved in 30 mL of toluene. After degassing of the mixture and saturation with argon gas, freshly recrystallized AIBN (12.00 mg) was added and the solution was allowed to stir for 24 h at 80 °C. The mixture was diluted with 10 mL of toluene and the polymer was precipitated by rapid injection of the reaction mixture into 200 mL of methanol. The polymer was collected by filtration and dried *in vacuo* to yield a white solid (1.35 g, 43%).

¹H NMR (300 MHz, CDCl₃) δ 7.92–8.21 (m), 6.91–7.42 (m), 5.85–6.85 (m), 4.85–5.49 (m), 4.05–4.55 (m), 3.16–3.49 (m), 0.86–1.34 (m).

2.2.4. Synthesis of CzEh-PPV

This polymer was prepared according to the procedure we reported previously [20]. The molecular weight of the polymer determined by GPC is $\bar{M}_n = 53,500$ and $\bar{M}_w = 122,000$.

3. Instrumental analysis

¹H NMR spectra were recorded on a Varian Mercury NMR 300 and 400 MHz spectrometer using deuterated chloroform (CDCl₃*d*) purchased from Cambridge Isotope Laboratories, Inc. Molecular weights of the copolymer, VCz-Ox and CzEh-PPV was determined by gel permeation chromatography (GPC, Waters) using polystyrene as a standard and THF as an eluent.

Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821^e instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 thermal analysis system under a heating rate of 10 °C/min.

Absorption spectra of film samples were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 190–1100 nm.

3.1. Sample preparation for investigating photoreaction

Copolymer films were prepared by spin-coating the solutions in monochlorobenzene onto a quartz substrate. In the solid state devices, the crosslinkable hole conducting copolymer, VCz-Ox was dissolved in monochlorobenzene, 2 wt.% of the cationic photoinitiator [4-[(2-hydroxytetradecyl)oxy]-phenyl]phenyliodonium hexafluoroantimonate was added and finally the solution was spin-coated on a desired substrate. The films were exposed to UV-light ($\lambda_{max} = 254$ nm, power = 40 mW/cm²) for 10 s at 100 °C. In order to investigate the solvent resistivity by using UV-vis absorption spectroscopy, the exposed films were rinsed using THF as a solvent and the spectrum was taken again.

3.2. Electroluminescence measurement

The multilayer PLEDs have structures of ITO/PEDOT:PSS(20 nm)/ CzEh-PPV(30 nm)/LiF(1 nm)/Al(100 nm) [Device A], ITO/PEDOT:PSS (20 nm)/VCz-Ox(20 nm)/CzEh-PPV(30 nm)/LiF(1 nm)/Al(100 nm)[Device B], and ITO/VCz-Ox(20 nm)/CzEh-PPV(30 nm)/LiF(1 nm)/ Al(100 nm) [Device C]. Three different device geometries were employed for evaluating the function of VCz-Ox polymer layer (see Fig. 3(a)). The conducting poly(ethylene dioxythiophene):poly(styrene sulfonate)(PEDOT:PSS) layer was spin-coated onto the indium tin oxide (ITO)-coated glasses in an argon atmosphere. In device B, VCz-Ox solution in monochlorobenzene was spin-coated on PEDOT:PSS layer and the atop layer was exposed to the UV light (λ = 254 nm). The green-emitting CzEh-PPV layer then was spin-coated onto the thoroughly dried PEDOT layer using the solution (conc.: 1 wt.%) in monochlorobenzene. In device C, PEDOT: PSS layer was omitted from the structure of device B. For multilayer devices, LiF (1 nm)/Al(100 nm) electrodes were deposited onto the CzEh-PPV layer under the same condition. I-V characteristics were measured using an assembly consisting of dc power supply (Hewlett-Packard 6633B) and a digital multimeter (Hewlett-Packard 34970A). Luminance was measured by using a Minolta LS-100 luminance meter. The thickness of the material layer was determined by a TENCOR P-10 surface profilometer.



Scheme 1. Polymerization of 9-(4-vinyl-benzyl)-9H-carbazole (1) and 3-methyl-3-(4-vinyl-benzyloxymethyl)-oxetane (2) to yield the copolymer VCz-Ox (*m*:*n* = 1:1). The structure of CzEh-PPV that is used as a light-emitting material.

4. Results and discussion

4.1. Synthesis

A simple synthetic route to the photoreactive copolymer VCz-Ox and the structure of CzEh-PPV are depicted in Scheme 1. A new hole-conducting copolymer was prepared by the radical polymerization of 9-(4-vinyl-benzyl)-9*H*-carbazole (1) and 3-methyl-3-(4-vinyl-benzyloxymethyl)-oxetane (2). 9-(4-Vinyl-benzyl)-9*H*-carbazole (1) was prepared by the reaction of carbazole with 1-chloromethyl-4-vinyl-benzene in DMF. The reaction mixture was precipitated in water and neutralized with aqueous HCl. The product was obtained as a white powder in the 74% yield. 3-Methyl-3-(4-vinyl-benzyloxymethyl)-oxetane (2) was also prepared from (3-methyl-oxetan-3-yl)-methanol and 1chloromethyl-4-vinyl-benzene by using the same procedure as that described above. A viscous liquid was also obtained in the 70% yield.

Two monomers were successfully synthesized in a very good yield. This simple synthesis of two monomers leads to a very efficient yield of the resultant copolymer. All the intermediates and the resultant copolymer were characterized well by ¹H NMR analysis. By using the NMR analysis, we could determine the ratio of the two monomers (monomer 1:monomer 2 = 1:1).

Further, the molecular weights of the photoreactive copolymer and CzEh-PPV were determined by gel permeation chromatography (GPC, Waters) with polystyrene as a standard and THF as an eluent. The number- and weight-average molecular weights of the copolymer VCz-Ox obtained by using the GPC analysis are 8500 and 16,000, respectively. Moreover, the molecular weights of CzEh-PPV are determined to be $\bar{M}_n = 53$, 500 and $\bar{M}_w = 122$, 000.



Fig. 1. Thermal analysis of VCz-Ox. (A) DSC thermogram: (a) before photocuring, (b) after photocuring; (B) TGA thermogram.



Fig. 2. Solvent resistivity test by means of UV-vis spectroscopy (cationic photoinitiator: 2 wt.%, curing time: 10 s, and light intensity: 40 mW/cm²). (A) Before UV exposure. (B) After rinsing the exposed film with THF.

4.2. Physical properties of the photoreactive polymer

4.2.1. Thermal analysis of the photocrosslinkable copolymer VCz-Ox

We investigated the thermal properties of the newly synthesized photoreactive copolymer by using differential scanning calorimetry (DSC) and TGA under a nitrogen atmosphere.

The glass transition temperature (T_gs) of VCz-Ox is 115 °C (see Fig. 1A(a)). No discernible melting behavior up to 290 °C was observed in the DSC thermogram of the copolymer. After the UV irradiation of the film containing 2 wt.% of a cationic initiator, there was no significant T_g which can be observed in the effective temperature window (see Fig. 1A(b)).

In the TGA thermogram of the copolymer, no significant weight loss was observed up to $300 \,^{\circ}$ C. The onset temperature of the primary decomposition was above $395 \,^{\circ}$ C.

4.2.2. Solubility test after UV-light irradiation

The synthesized copolymer, VCz-Ox, is readily soluble in common organic solvents like toluene, chloroform, and THF. After UV illumination, it became completely insoluble. UV–vis absorption spectroscopy was used to test the efficiency of the crosslinking process. The absorption spectra of crosslinked copolymer layers before and after rinsing the film with THF were compared (rinsing condition: THF for 1 min). Considering the conditions for device fabrication by the UV illumination for a short period, the curing processes at both 50 and 100 $^{\circ}$ C were carried out to soften the film and to enhance the efficiency of crosslinking.

Fig. 2 shows the results of the solubility test for the crosslinked copolymer. The film was crosslinked by photocuring at 50 and 100 °C for 10 s. After low-temperature curing (at 50 °C), 75% of the initial absorbance was observed; UV curing at 100 °C resulted in solvent resistivity of up to 100% (see Fig. 2(B)). This demonstrates the advantage of using the new oxetane-containing copolymer as an insoluble hole-transporting material.

4.3. Electroluminescence of a multilayered device

We could fabricate high-quality films by spin-coating the solutions of VCz-Ox and CzEh-PPV for PLED systems. Green-emitting CzEh-PPV was employed as an emissive material in multilayered devices [20]. A thin film of PEDOT:PSS was deposited on ITO as the anode for facilitating hole injection. Then, we fabricated three different devices (see Fig. 3(a)); Device A has a light-emitting polymer layer directly on the surface of the PEDOT:PSS layer. In Device B, we spin-coated the VCz-Ox polymer on the PEDOT:PSS layer. Device C does not have a PEDOT:PSS layer but only has the VCz-Ox layer. The VCz-Ox films were all cured by UV illumination during the fabrication of the PLEDs. Sequentially, CzEh-PPV was spin-coated on the photo-cured VCz-Ox film. We did not observe the deterioration of the surface of the cured VCz-Ox film by applying the solution of CzEh-PPV; this can be evidenced by the results of the UV-vis absorption spectroscopy.

The current–voltage–luminance curves of the two different PLEDs are shown in Fig. 3(b). The forward current is observed to increase significantly after the turn-on voltage was exceeded. The turn-on voltages (electric fields) of the two PLEDs were relatively high. In particular, Devices B and C, that is, devices with the VCz-Ox layer, have relatively higher turn-on voltage than Device A. This indicates that the increase in turn-on voltage is due to the high dielectric nature of the VCz-Ox layer.

The higher turn-on voltage of Device B is explained by the fact that the two layers for hole injection and transport have a higher energy barrier for carrier migration.

Further, the maximum brightness of the PLEDs was in the range of 1150 cd/m² (at 144.8 mA/cm²) for Device A to 2450 cd/m² (at 295.3 mA/cm²) for Device B. The maximum luminous efficiencies of Devices A, B, and C were determined to be 0.86 cd A⁻¹ (at 57.88 mA/cm²), 0.76 cd A⁻¹ (at 5.79 mA/cm²), and 0.99 cd A⁻¹ (at



Fig. 3. (a) Device configurations of three PLEDs. (b) Dependence of current density and luminance on the applied voltage. Sample: Device A (circle), Device B (square), and Device C (triangle); current density (filled symbol) and luminance (open symbol).

Table 1	
Measured parameters of PLEDs fabricated with VCz-Ox	photoreactive hole-transport materials

Device	Turn-on (V)	Maximum luminance, cd m ^{-2} (corresponding <i>J</i>)	Maximum luminous efficiency, cd A ⁻¹ (corresponding <i>J</i>)	Maximum power efficiency, lm W ⁻¹ (corresponding J)
A	5	1150(144.78)	0.86 (57.88)	0.22 (26.53)
В	25	2450(295.29)	0.76 (5.79)	0.11 (0.23)
С	19	1581 (270.33)	0.99 (31.12)	0.10(1.35)



Fig. 4. Dependence of luminous efficiency on current density. Sample: Device A (circle), Device B (square), and Device C (triangle).

31.12 mA/cm²), respectively. Detailed device performance is summarized in Table 1.

It should be noted that the luminous efficiencies of all three samples are comparable, and the stabilities are quite persistent particularly at a high current density (>175 mA/cm²) in Devices B and C (see Fig. 4).

In other words, the new photoreactive HTM exhibited reasonably good performance as a hole-transport material in Devices B and C. In Device B, we could observe slightly improved luminous efficiency and brightness; this indicates that the hole-transporting property of photo-cured VCz-Ox has good potential to lessen the energy difference between the HOMOs of PEDOT:PSS and CzEh-PPV layers. It can also be assumed that the higher external quantum efficiency is attributed to the well-balanced hole-transporting properties and electron-transporting capabilities of the PLEDs used herein. Although overall device performances are not comparable to the reported data, we could figure out the applicability of new polymer for a hole-transporting layer in PLEDs.

5. Conclusion

A novel polymeric hole-transport material based on carbazole with the ability to transport charge in the polymer backbone has been synthesized. The copolymer VCz-Ox contains a monomer bearing an oxetane group that is used to photocrosslink the spincoated layers by UV illumination. Multilayer organic light-emitting diodes fabricated from VCz-Ox and a green-emissive CzEh-PPV material exhibited reasonable device performance, which implies that the photo-cured VCz-Ox materials have promising hole-transporting ability.

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