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Research Article

Side-Chain Polyimides as Binder Polymers for Photolithographic Patterning of a Black Pixel Define Layer for Organic Light Emitting Diode

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A pixel define layer (PDL) in an organic light emitting diode (OLED) is patterned using a photolithographic process before the deposition of organic layers on top of ITO anode. If the patterning of PDL on OLED panels can be achieved using a black photoresist, the patterning of black matrix (BM) on top of PDL patterns can be omitted by reducing the reflection of ambient light from OLED panels. In this study, we synthesized a series of side-chain-type polyimides as binder polymers of black photoresists and investigated the potential of using the black photoresist for the fine patterning of black PDL on OLED panels.

1. Introduction

Organic light emitting diodes (OLEDs) have become one of the major trends in the fabrication of flat panel displays because of their advantages, such as light weight, slim panels, fast response time, wide viewing angle, high resolution, and low power consumption [1-4]. The light emitting area of an OLED device is disposed at the luminous region of the pixel array on the OLED panel connected to a thin film transistor unit. Before the deposition of OLED organic layers, a pixel define layer (PDL) is patterned via a photolithographic process, as shown in Figure 1 [5-8].

Currently, positive-tone photosensitive polyimide [9, 10] is used to fabricate PDL microstructures. The corresponding PDL is yellowish brown similar to that of polyimide films. Since the yellowish-brown polyimide layer of PDL reflects the incident light, the visibility of the OLED display is reduced, particularly when used outdoors. Therefore, in the current positive-tone photolithographic process, a black matrix (BM) layer is patterned on top of the PDL pattern to improve the visibility of the OLED device (Figure 1).

If the patterning of PDL on OLED panels can be achieved using a negative-tone black photoresist [11] containing black pigment instead of the positive-tone photoresist based on photosensitive polyimide, the photolithographic process of patterning BM on top of the PDL pattern would be omitted. The required components for a typical negative-tone black photoresist include the photoinitiator, photosensitizer, multifunctional monomer, black pigment millbase, and binder polymer developable with aqueous alkaline solution. The binder polymer is crucial in the patterning of black PDL on OLED panels. It is not only one of the major components in terms of weight but also affects the shape of PDL patterns during its development in the photolithographic process. The process temperature of OLED panel fabrication reaches close to 300 °C, including the postcure step after photolithographic patterning of PDL; therefore, the thermal stability of the binder polymer

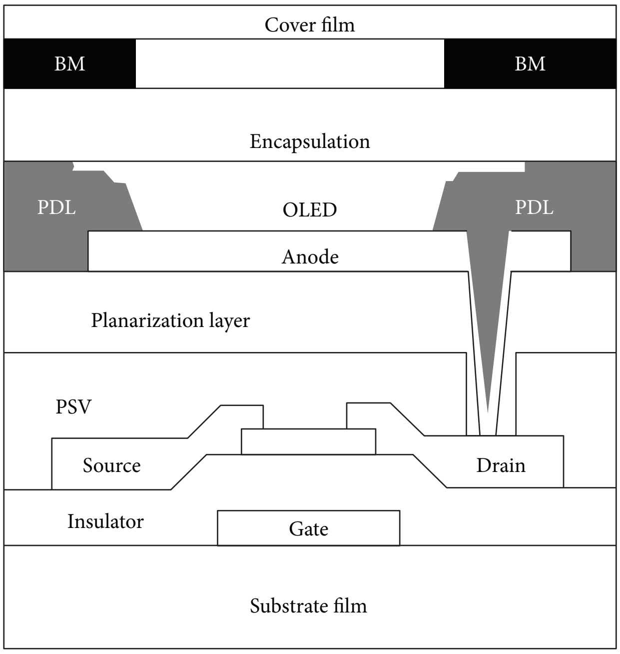


Figure 1: Typical cross-sectional view of an OLED panel.

should also be considered. Herein, new binder polymers with thermally stable imide linkages were synthesized and applied to the black photoresist formulation to pattern black PDL on OLED panels.

2. Experimental Methods

2.1. Materials and Characterization. Chemicals and solvents were reagent grades and used without further purification: poly(styrene-*co*-maleic anhydride), cumene terminated, $M_n \sim 1600$ (PSMA); 5-aminoisophthalic acid (AIPA); 3,5-bis(trifluoromethyl) aniline (6FAL); 4-aminostyrene (AS); 2-hydroxylethylacrylate (2-HEA); glycidyl methacrylate (GMA); dimethyl acetamide (DMAc); 3,5-di-*tert*-4-butylhydroxytoluene (BHT); tetrabutylphosphonium bromide (TBPB); propylene glycol monomethyl ether acetate (PGMEA); and pentaerythritol triacrylate (PETA).

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 thermogravimetric analyzer with a programmed temperature at 10 °C/min. Fourier-transform infrared spectroscopy (FT-IR) was performed on a Varian 670/620 spectrometer using the KBr pellet method. ^{1}H NMR spectroscopy was taken on a Bruker AVANCE III HD 400 MHz spectrometer.

2.2. Synthesis of Styrene-Type Side-Chain Polyimides. PSMA (20 mmol based on maleic anhydride units) was dissolved in 20 mL of DMAc. Varying molarities of AS, AIPA, and 6FAL were added sequentially once every hour and stirred at room temperature. After the formation of amic acid linkages between maleic anhydride units of PSMA and three aromatic amines (AS, AIPA, and 6FAL), a free radical polymerization inhibitor (BHT) and a chemical imidization agent (acetic anhydride; 10 mL) were added and the reaction mixture was reacted for 4.5 h at 100 °C to afford side-chain polyimides (PSI-x) [12] (Figure 2). After cooling down, the reaction mixture was poured into excess water (>10× volume) and the precipitates were collected by centrifugation. EtOAc was added to the precipitates, and the insoluble was removed via filtration. The organic solution was washed twice using brine, dried with anhydrous Na_2SO_4, and evaporated to dryness. The solid product was washed using diethyl ether multiple times to afford PSI series side-chain polyimide as brown powder.

2.3. Synthesis of Acrylate-Type Side-Chain Polyimides. PSMA (20 mmol based on maleic anhydride units) was dissolved in 20 mL of DMAc solvent. First, 2-HEA (10 mmol) and pyridine (1 mmol) were added to the PSMA solution and the reaction mixture was stirred at room temperature for 16 h. Second, 6FAL (10 mmol) was added and stirred at room temperature for 1 h. Acetic anhydride (10 mL) was added, and the mixture was stirred at 100 °C for 4.5 h for the imidization reaction to occur (Figure 3). After the reaction, the mixture was poured into excess amount of water. The subsequent procedure was the same as that of PSI series in Section 2.2 to afford PSEI series.

2.4. Synthesis of Methacrylate-Type Side-Chain Polyimides. PSMA (20 mmol based on maleic anhydride unit) was also dissolved in 20 mL of DMAc. AIPA (6 mmol) and 6FAL (14 mmol) were added sequentially once an hour and stirred at room temperature. The reaction mixture was heated to 130 °C and stirred for 16 h [13]. After cooling down, GMA (4 mmol), TBPB (0.4 mmol), and BHT (0.04 mmol) were added and stirred at 90 °C for another 3 h (Figure 4). The reaction mixture was poured into excess water. The subsequent procedure was the same as PSI series to afford PSEA-1.

For the PSEA-2 synthesis, PSMA was dissolved in PGMEA (net. 30 wt%) instead of DMAc, and the reaction was proceeded as above with GMA.

3. Results and Discussions

3.1. Synthesis of Polyimide-Based Binder Polymers. The use of negative-tone black photoresist, instead of positive-tone photoresist based on photosensitive polyimide could remove both the BM patterning and the 1/4λ polarizing film by reducing the reflection of ambient light from the OLED panel. Positive-tone photoresist based on photosensitive polyimide is used herein because the resulting PDL made of polyimide thin film has a high thermal stability and can withstand temperatures up to 300 °C during the OLED panel fabrication process. However, the positive-tone photoresist based on photosensitive polyimide cannot be used to develop a black photoresist due to limited penetration depth of the UV light in the photolithographic patterning of black PDL on the OLED panel. The negative-tone black photoresist has deeper penetration depth than positive-tone photoresist since the photolithographic patterning is performed via a crosslinking reaction mechanism involving free

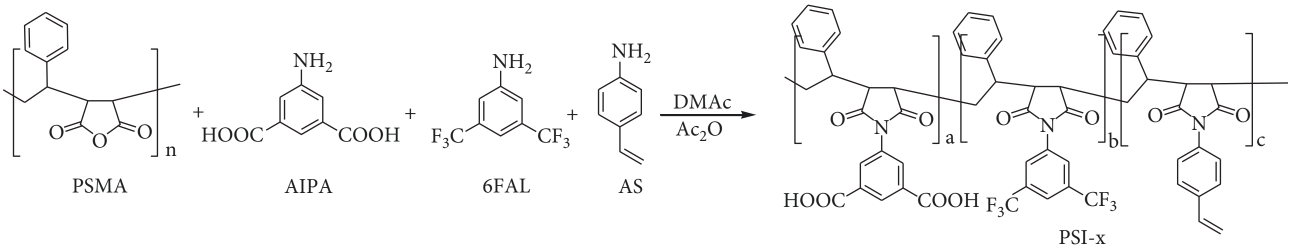


Figure 2: Synthetic scheme of styrene-type side-chain polyimides.

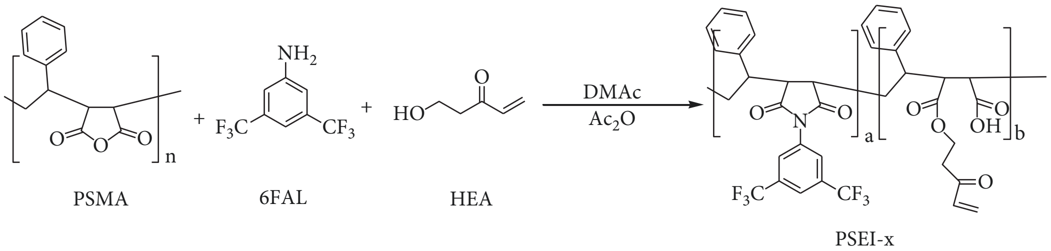


Figure 3: Synthetic scheme of acrylate-type side-chain polyimides.

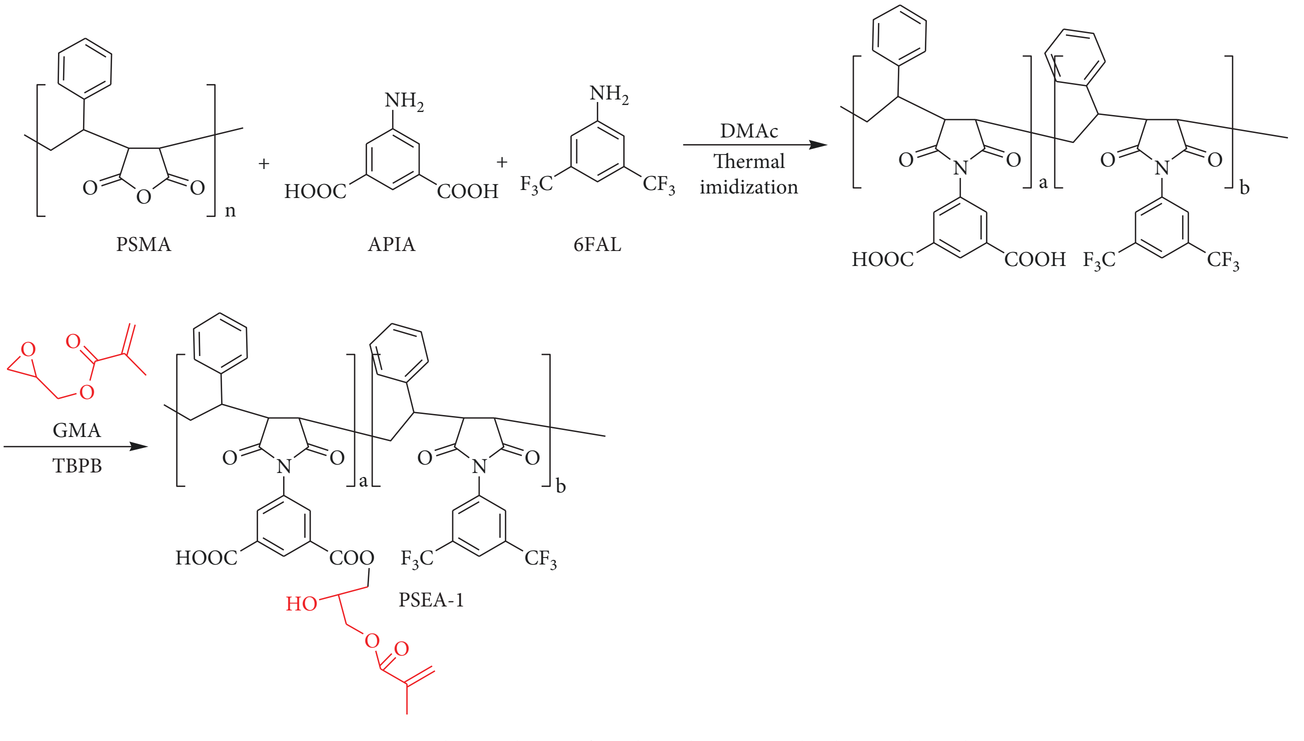


Figure 4: Synthetic scheme of methacrylate-type side-chain polyimides.

radical chain polymerization among multifunctional monomers and the binder polymer.

The binder polymer should have carboxylic groups to be developed easily with aqueous alkaline developer. Moreover, the binder polymer should also be crosslinked tightly with the multifuncional monomers upon UV light irradiation in order not to be soluble in the aqueous alkaline developer. Further, a high thermal stability of the binder polymer that corresponds to the photosensitive polyimide in the positive-tone photoresist is required. According to this guideline, three different binder polymers with thermally stable imide linkages have been synthesized.

3.1.1. PSI and PSEI Series. In the synthesis of PSI series binder polymers, three aromatic amines reacted with the maleic anhydride units of PSMA. The three amines (AIPA, 6FAL, and AS) were used to afford carboxyl groups required in the development step of photolithography. The solubility of the binder polymer in the PGMEA, a common solvent in the photoresist, was also examined. Besides, double bonds

Table 1: Synthesis of side-chain polyimides for binder polymers of black photoresists.

Binder polymer samples	Sample codes	Molarities (mmol)			Yield (%)	GPC M_w
		AS	AIPA	6FAL		
PSI series	PSI-1	4	6	10	52	4716
	PSI-2	4	8	8	44	4863
PSEI series		2-HEA		6FAL		
	PSEI-1	10	10	53	4637	
PSEA series		AIPA	6FAL	GMA		
	PSEA-1	6	14	4	56	4735
	PSEA-2	6	14	6	—	4819

responsible for the photocrosslinking reaction were also included through the AS monomer. In the synthesis of PSI series, the chemical imidization was carried out utilizing acetic anhydride under mild condition of 100 °C to avoid self-polymerization of AS via a thermal initiation mechanism. The PSI product was recovered by precipitation in excess water to remove the excess acetic anhydride followed by filtration, drying, and then tested in the black photoresist.

In PSEI series, 2-HEA was reacted with maleic anhydride units of PSMA to generate both carboxyl groups and double bonds. Then, aromatic amine (6FAL) was imidized using chemical imidization method under mild conditions. Because acetic anhydride was used for imidization, PSEI has to be worked-up in the same way as PSI series.

3.1.2. PSEA Series. PSEA series were synthesized using two different processes. First, APIA and 6FAL amines were reacted via thermal imidization with maleic anhydride groups of PSMA in DMAc solvent at 130 °C. Then side-chain polyimide intermediate was reacted with GMA to afford a PSEA-1 binder polymer, in which carboxyl groups were partially converted to epoxymethacrylates. The PSEA-1 sample was recovered in the same manner as PSI series. In the second process, PSEA-2 was synthesized using PGMEA solvent instead of DMAc. However, PSEA-2 was obtained using a one-pot solution method without work-up and was tested directly as the binder polymer in the photolithographic patterning of black PDL in the OLED panel.

Table 1 shows that the yields of polyimides were not high (44%–56%) because the polyimide products had relatively high carboxyl groups and underwent weight loss during precipitation in excess water. GPC, FT-IR, and ^{1}H NMR analyses of the PSEA-2 sample are shown in Figures 5, 6, and 7, respectively. The molecular weight of PSEA-2 ($M_w = 4819$ g/mol) was higher than that of PSMA ($M_n = 1600$ g/mol) due to the expansion of hydrodynamic volume after an imidization step that introduced bulky substituents in side chains of a relatively flexible PSMA polymer. According to FT-IR spectra, anhydrides were converted to imides and methacrylate esters. Moreover, ^{1}H NMR spectrum indicated that electron-poor aromatic amines (δ 8.18–8.45), epoxy (δ 4.16), and methacrylate groups (δ 1.87–1.96, 5.66, and 6.07) were introduced to PSMA chains.

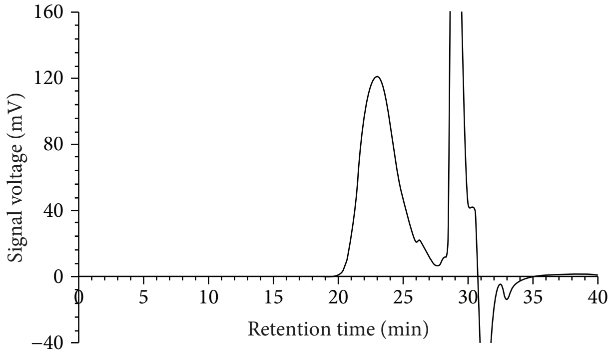


Figure 5: GPC chromatogram of PSEA-2 polyimide.

3.2. Photolithography and Thermal Stability of Black PDL Patterns. The black photoresist for the patterning of the black PDL of OLED panel is composed of the photoinitiator, photosensitizer, multifunctional monomer, polyimide as a thermal stabilizer, black millbase, and binder polymer. The binder polymer and multifunctional monomer are the main components of the photoresist, which affect the exact patterning of PDL via the photocrosslinking reaction in the UV-irradiated area and development of UV-unirradiated area by aqueous alkaline solution.

In this study, a commercial binder polymer SR-6300 (SMS Co., Korea) known as cresol novolac epoxyacrylate, dissolved in PGMEA solvent at 30 wt%, was used as a reference binder polymer as shown in Table 2. A commercial sample PETA was used as multifunctional monomer, which has the functionality of 3. The thermal stability of the reference black photoresist (PT-0), determined by TGA, was not high enough (up to 300 °C) to endure the photolithographic patterning of PDL even after the subsequent postcure treatment at 250 °C for 30 minutes.

Figure 8 shows the photolithographic patterns of the black PDL using the side-chain polyimide binder polymers. The black photoresists PT-0 and PT-3 exhibited fine patterns of black PDL. However, PT-1 and PT-2 showed irregular or wavy PDL patterns. In case of PT-1 photoresist PSI type binder polymer had styrenic groups as source of double bonds for the photocrosslinking reaction, so that the adhesion to the silicon wafer was not as good as the reference binder polymer (SR-6300), which has epoxy acrylate as a source of double bonds. In the case of the PT-2 black photoresist, the wavy PDL pattern was related to the high acid value of the binder polymer PSEI-1 in which acrylate groups were introduced via the reaction of 2-HEA with maleic anhydride units of PSMA. High amount of 2-HEA monomer had to be used for the complete solubility of the resulting PSEI-1 in PGMEA. The PT-3 black photoresist showed fine PDL patterns due to the balance of good adhesion to the silicon wafer and the optimum acid value from benzoic acid-type carboxyl groups.

The effect of side-chain polyimide binder polymers on the thermal stability of the resulting PDL patterns was evaluated via TGA analysis. The black PDL patterns formed on the silicon wafer were scratched off after photolithographic

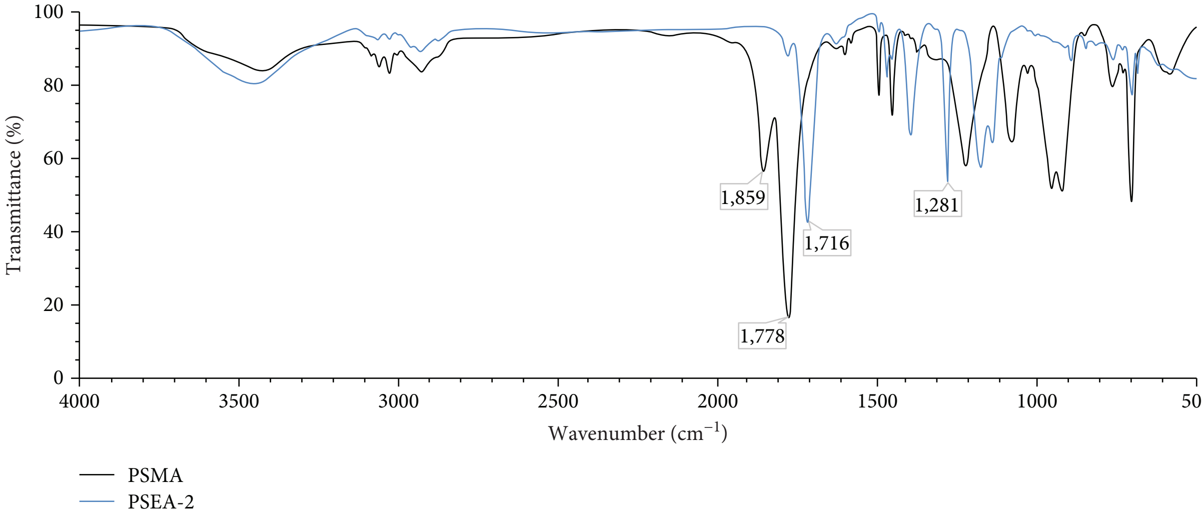


FIGURE 6: FT-IR charts of PSEA-2 and its starting material PSMA.

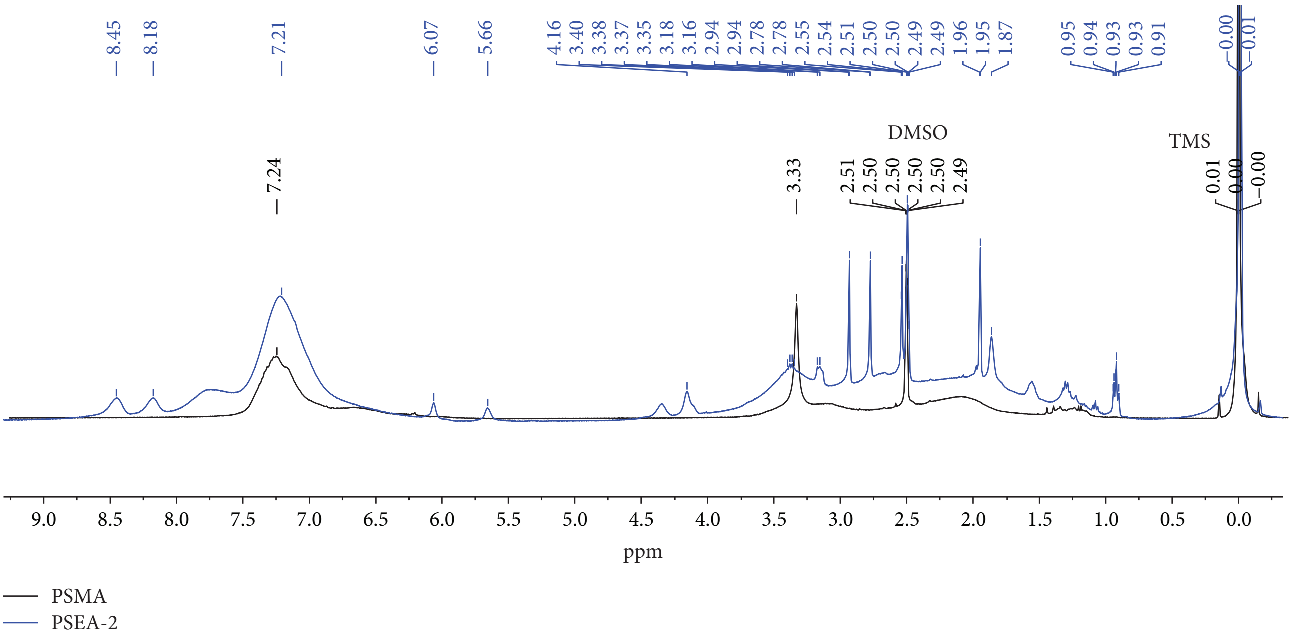


FIGURE 7: ^{1}H NMR diagrams of PSEA-2 and its starting material PSMA in d_6-DMSO.

patterning using a sharp razor blade, and the fine black powder was subjected to TGA analysis. As shown in Table 2 and Figure 9, the PT-3 photoresist having thermally stable side-chain polyimide PSEA-2 as a binder polymer exhibited higher 1 wt% loss temperature than the PT-0 reference photoresist which had commercial SR-6300 as binder polymer.

4. Conclusion

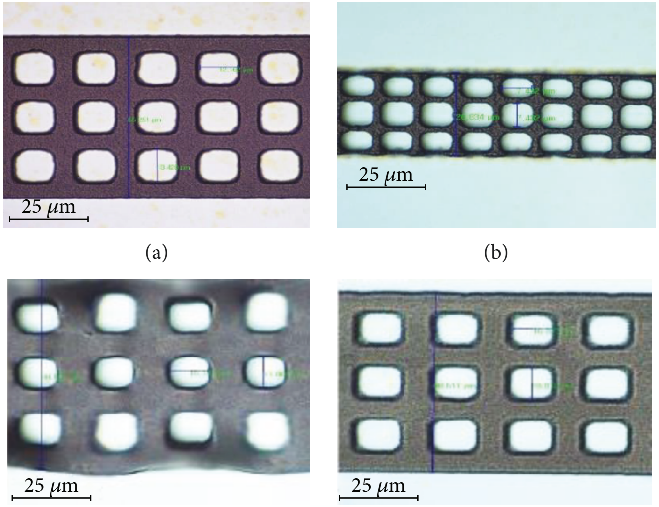
In this study, a series of new binder polymers having thermally stable side-chain imide linkages were synthesized and used in the black photoresist formulation to pattern black PDL on the OLED panel. For the synthesis of binder polymers, poly(styrene-*co*-maleic anhydride) was used as the starting material and three different types of side-chain polyimides were obtained. The epoxy methacrylate-type side-chain polyimide afforded a fine black PDL pattern with high thermal stability, comparable to that of the currently used positive-tone photosensitive polyimide.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Table 2: Formulation of black photoresists and thermal stability of a black PDL pattern [14].

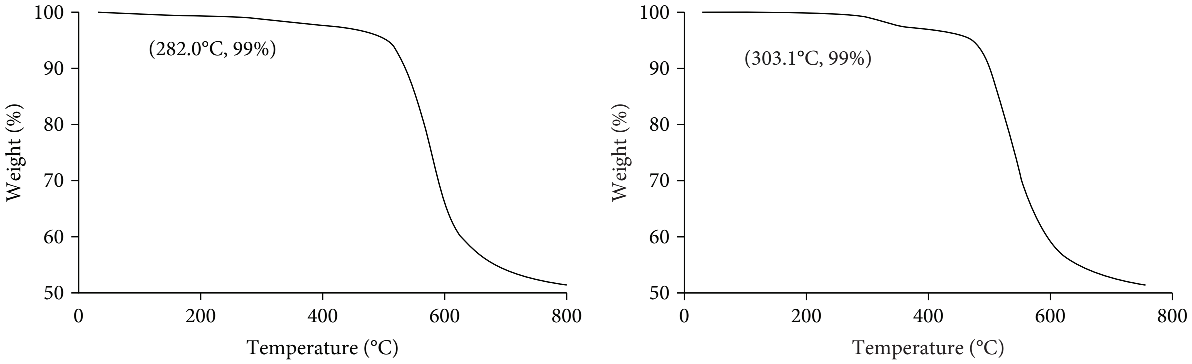
Components/photoresist samples		PT-0	PT-1	PT-2	PT-3
Photoinitiators	Irgacure 754	1	1	1	1
	Irgacure TPO	6	6	6	6
Photosensitizer	Darocure ITX	2	2	2	2
Binder polymer (30 wt% in PGMEA)	SR-6300	35			
	PSI-2		35		
	PSEI-1			35	
	PSEA-2				35
Multifunctional monomer	PETA	8	8	8	8
Polyimide thermal stabilizer (30 wt% in PGMEA)	MY-10	10	10	10	10
Black millbase (23 wt% in PGMEA)	LT-1 (SKC htm Co., Korea)	35	35	35	35
Solvent	PGMEA	5	5	5	5
Total	wt%	100	100	100	100
Thermal stability	1 wt% loss temp. (°C, TGA)	282	—	—	303



(a) (b)

(c) (d)

Figure 8: The optical microscopic images of black PDL patterns obtained with (a) PT-0, (b) PT-1, (c) PT-2, and (d) PT-3 black photoresists.



(a) (b)

Figure 9: TGA thermograms of black powders obtained from the black PDL patterns. (a) PT-0 and (b) PT-3.

Disclosure

Part of this work's content will be used on "The 18th International Meeting on Information Display (IMID)" to be held on Aug. 29, 2018.

Conflicts of Interest

The authors declare that they have no competing interests.

Acknowledgments

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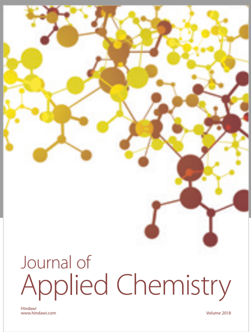
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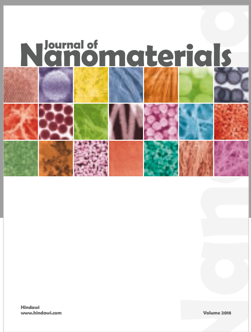
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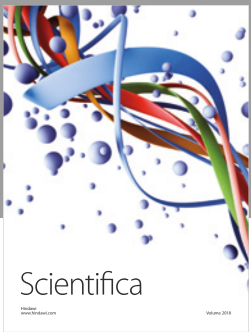
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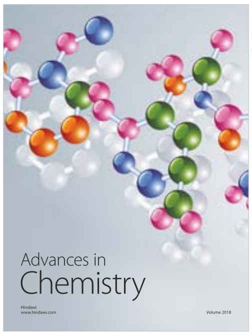
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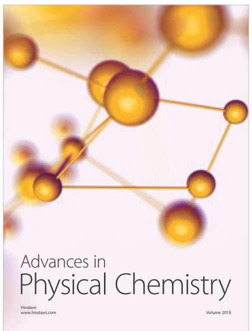
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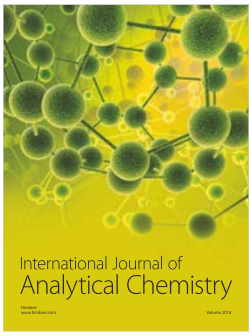
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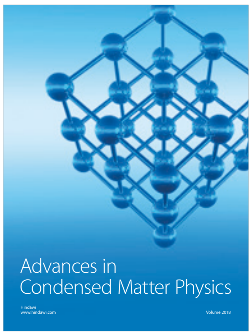
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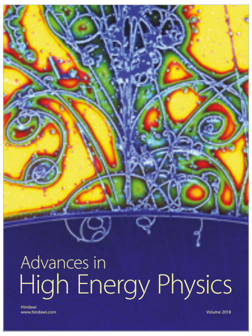
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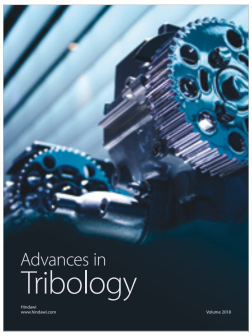
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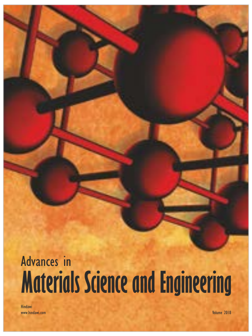
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