

Synthesis of New Binder Polymers for Photolithographic Patterning of Black Pixel Define Layers of Organic Light Emitting Diode

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How to cite this paper: Shi, G., Baek, K., Ahn, S.H., Bae, J., Kim, J. and Park, L.S. (2019) Synthesis of New Binder Polymers for Photolithographic Patterning of Black Pixel Define Layers of Organic Light Emitting Diode. *Materials Sciences and Applications*, 10, 387-396.

<https://doi.org/10.4236/msa.2019.1011049>

Received: October 1, 2019

Accepted: November 8, 2019

Published: November 11, 2019

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Abstract

The fabrication of black pixel define layer (PDL) on the organic light emitting diode (OLED) panel has been developed actively by using negative-tone black photoresist which contain photoinitiator, photosensitizer, binder polymer, multifunctional monomer and black mill base in order to improve the outdoor visibility of OLEDs. Cardo type binder polymer containing bulky and rigid fluorene group has been widely used in the black photoresist formulation. However, the commercial cardo binder polymer has high cost and requires high UV dose for the fine patterning of PDL in the photolithographic process. In this study we designed and synthesized various non-cardo type binder polymers and evaluated the new binder polymers in comparison with the cardo binder polymer for the improved patterning of PDL on the OLED panel.

Keywords

Organic Light Emitting Diode, Pixel Define Layer, Photolithography, One-Pot Synthesis

1. Introduction

Organic light-emitting diodes (OLEDs) have been widely applied to the small size mobile devices, large OLED TVs and flexible OLED panels, because of such merits of OLEDs as fast response time, low operating voltage, wide viewing angle as well as light weight and thin-film features [1] [2] [3] [4]. One OLED pixel in small size OLEDs is able to emit red (R), green (G), and blue (B) light from separate sub-pixels fabricated by the photolithographic process with a fine pat-

terned mask. Although the visibility of OLED is better than that of LCD due to much higher contrast [5] [6] [7], the further improvement of its visibility is still highly desirable, especially for the outdoor use of mobile and wearable OLED devices. One simple technique is to reduce the reflected ambient light by circular polarization, and an alternative way is to locate a light-absorbing black layer at the back of OLED [8].

The photoresist based on positive-tone photosensitive polyimide has been used to fabricate the pixel define layer (PDL) of OLED panel for the small-size OLED devices, which is able to exhibit good resolution and high contrast [9]. In order to further improve the visibility of OLEDs, the black photoresist based on negative-tone photosensitive system has been studied actively [10] [11]. A typical negative-tone black photoresist consisted of photoinitiator, photosensitizer, binder polymer, multifunctional monomer and black mill base, which makes the color of patterned PDL black to reduce the reflection of ambient light from the OLED panel. Of the components of black photoresist the binder polymer is very important since it determines the quality of the PDL patterns which are in the range of less than $10 \times 10 \mu\text{m}$ size on the OLED panel.

The so-called cardo-type binder polymer has been widely used in the negative-tone black photoresist. The synthesis of a typical cardo binder polymer is shown in **Figure 1**.

As shown in **Figure 1**, the cardo binder polymer (CBP) has cardo carbon (marked with asterisk) in every repeat unit in the main chain of the binder polymer. The presence of the cardo carbons in the CBP contributes to the thermal stability of the final PDL patterns due to the rigid cyclic structure of the cardo moiety in the binder polymer. However such a structure of cardo binder polymer also reduces the double bond density (DBD) of the repeat unit which can be represented by the unit of mmol of double bonds per gram of repeat unit, *i.e.*, polymer (mmol/g). This is caused by the high molecular weight of the fluorene epoxy acrylate monomer with cardo carbon compared to the non-cardo type binder polymers. This effect of high DBD in the cardo binder polymer reduces the UV light sensitivity of the black photoresist, thus leading to difficulty in the production of fine patterned PDL in the photolithographic process.

In this study we tried various different synthetic methods to obtain non-cardo type binder polymers and evaluated these new binder polymers in the photolithographic process to obtain improved PDL patterns of the OLEDs.

2. Experimental

2.1. Materials

The non-cardo binder polymers were synthesized by reaction between diepoxide and monoacids to form diol intermediates, followed by reaction with dianhydrides (with/without external diol as co-monomer) to obtain the final acidic polyester type non-cardo binder polymers. The chemical names, code names and structures of diepoxides, monoacids and diols are shown in **Table 1**. All chemicals were reagent grades and subjected to reaction without further purification.

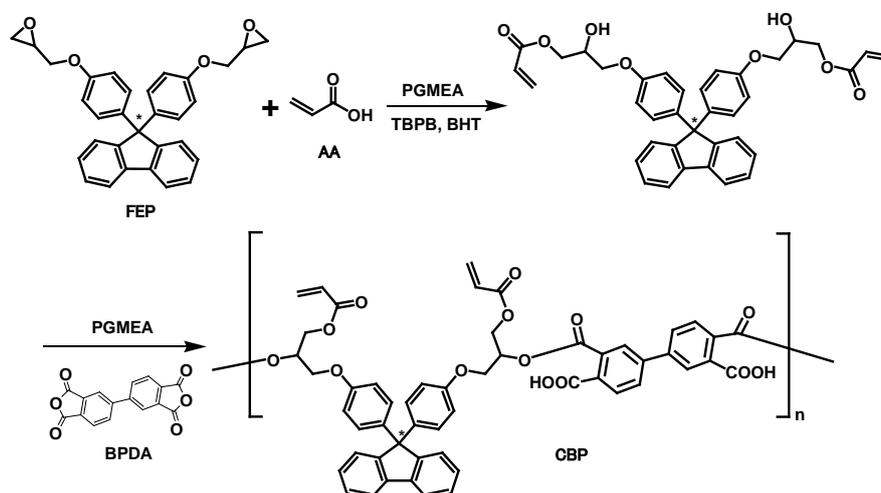


Figure 1. A typical synthetic scheme of cardo binder polymer (CBP).

2.2. Synthesis of Non-Cardo Binder Polymers of BP-1-x Series

Under nitrogen atmosphere, 5 mmol of **CHEP** diepoxide, 11 mmol of **AA**, 0.025 mmol of polymerization inhibitor **BHT**, 0.05 mmol of catalyst **TBPB** and certain amount of PGMEA solvent (40 wt% solid) were mixed at the same time and magnetically stirred (600 rpm) under 110°C for 3 h. After cooling, 5 mmol of 6FDA were added with extra PGMEA (40 wt% solid) and continued stirring at 110°C for another 3 h. The final product **BP-1-1** in clear solution was cooled down and directly used without work-up. Binder polymers synthesized with **JEP**, **REP**, **SIEP** and **BEP** as diepoxides were obtained by same procedure and the products were given code names of **BP-1-2** ~ **BP-1-5** respectively (**Figure 2**).

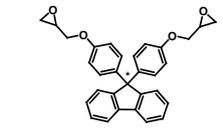
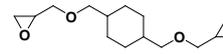
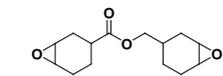
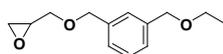
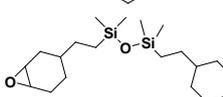
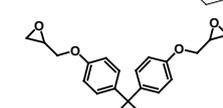
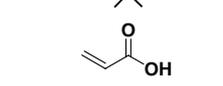
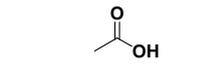
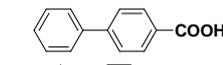
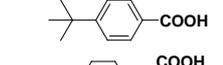
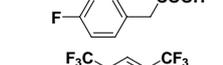
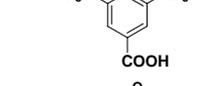
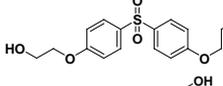
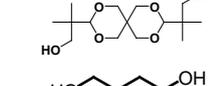
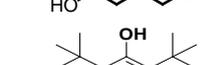
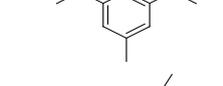
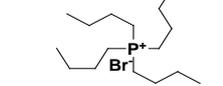
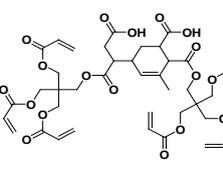
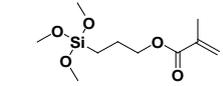
2.3. Synthesis of Co-Monoacid Type Non-Cardo Binder Polymers of BP-2-x Series

Under nitrogen atmosphere, 5 mmol of **CHEP**, 5.5 mmol of **AA**, 5.5 mmol of **AcOH** monoacid, 0.0125 mmol of inhibitor **BHT**, 0.05 mmol of catalyst **TBPB** and certain amount of PGMEA solvent (40 wt% solid) were mixed at the same time and magnetically stirred (600 rpm) under 110°C for 3 h. After cooling, 5 mmol of 6FDA were added with extra PGMEA (40 wt% solid) and continued stirring at 110°C for another 3 h. The final clear solution was cooled down and used directly without work-up. Binder polymers synthesized from **CHEP** diepoxide and **AcOH**, **PBA**, **TBBA**, **FPAC** and **6FB** as co-monoacids were coded as **BP-2-1**~**BP-2-5** respectively (**Figure 3**).

2.4. Synthesis of Co-Diol Type Non-Cardo Binder Polymers of BP-3-x Series

Under nitrogen atmosphere, 3 mmol of **SIEP**, 6 mmol of **AA**, 0.015 mmol of inhibitor **BHT**, 0.05 mmol of catalyst **TBPB** and certain amount of PGMEA solvent (40 wt% solid) were mixed at the same time and magnetically stirred (600 rpm) under 110°C for 3 h to obtain **SIEA** intermediate. After cooling, 2.5 mmol

Table 1. List of diepoxide, monoacid, diol reactants and selective photoresist components.

Code Name	Chemical Name	Structure
FEP	9,9-Bis(4-glycidyloxyphenyl)fluorene	
CHEP	1,4-Cyclohexanedimethanoldiglycidylether	
JEP	3,4-Epoxy cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate	
REP	Resorcinol diglycidylether	
SIEP	1,3-Bis[2-(7-oxabicyclo[4.1.0]heptan-3-yl)ethyl]-1,1,3,3-tetramethyldisiloxane	
BEP	Bisphenol a diglycidyl ether	
AA	Acrylic acid	
AcOH	Acetic acid	
PBA	Biphenyl-4-carboxylic acid	
TBBA	4-tert-Butylbenzoic acid	
FPAC	4-Fluorophenylacetic acid	
6FB	3,5-Bis(trifluoromethyl)benzoic acid	
SDO	Bis[4-(2-hydroxyethoxy)phenyl] Sulfone	
XDO	3,9-Bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane	
4DO	1,4-Butanediol	
BHT	2,6-di-tert-butyl-4-methylphenol	
TBPB	tetrabutylphosphonium bromide	
PM6	*Acidic multifunctional monomer*	
MSMA	3-(trimethoxysilyl) propyl methacrylate	

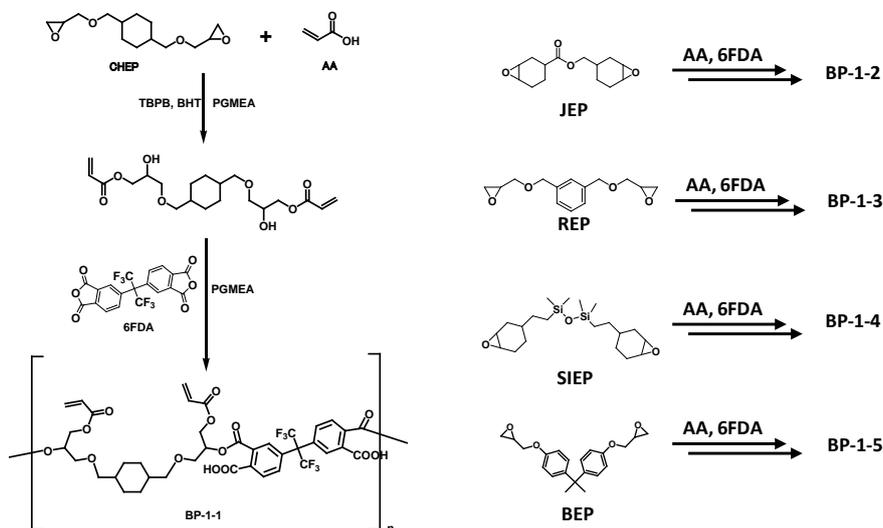


Figure 2. Synthetic scheme of representative non-cardo binder polymer **BP-1-x** series.

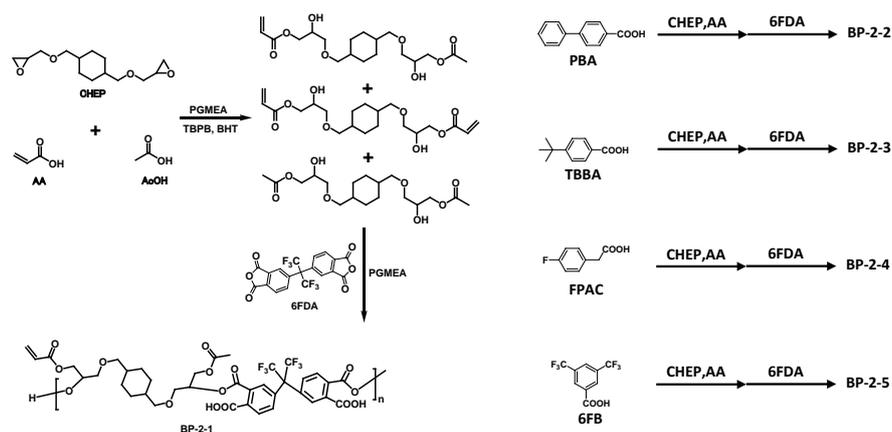


Figure 3. Synthetic scheme of representative co-monoacid type non-cardo binder polymer **BP-2-x** series.

of external diol **SDO** and 2.5 mmol of **6FDA** were added with extra PGMEA (40 wt% solid) and continued stirring at 110°C for another 3 h. The final product **BP-3-1** in clear solution was cooled down and directly used without work-up. Non-cardo binder polymers synthesized from **SDO**, **XDO**, and **4DO** as co-diols are coded as **BP-3-1** ~ **BP-3-3** respectively (**Figure 4**).

3. Results and Discussions

3.1. Synthesis and Analysis of Non-Cardo Binder Polymers

The synthesis of typical non-cardo binder polymers were conducted by similar process as the cardo binder polymer (**CBP**) in **Figure 1**. First, diepoxide were reacted with acrylic acid to obtain diol intermediate with acrylate double bonds. Second, the diol monomer was reacted with dianhydride to give the final acidic polyesters type product, *i.e.*, non-cardo binder polymer without cardo carbon moiety.

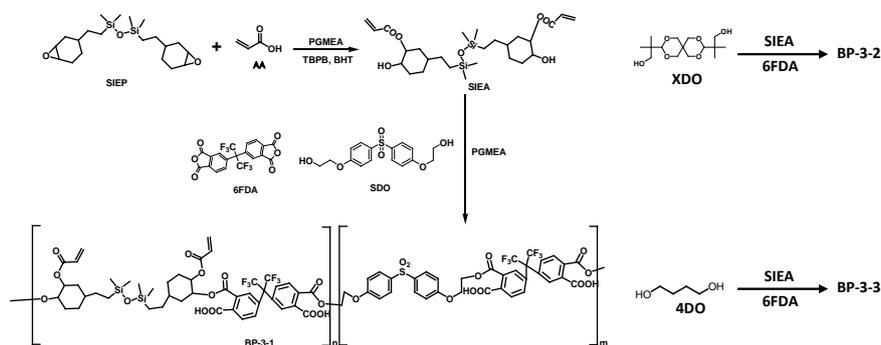


Figure 4. Synthetic scheme of representative co-diol type non-cardo binder polymer **BP-3-x** series.

One variation of the non-cardo binder polymer was the synthesis of co-monoacid type polymers for the reduction of acrylate DBD to regulate the photo-cross linking reaction in the photolithographic process. The other variation was the synthesis of co-diol type non-cardo binder polymers for the same purpose. It is noted that these syntheses of non-cardo binder polymers was one-pot reaction, in other word, the final non-cardo binder polymer solutions were all obtained in one reactor without separation of any intermediates or byproducts, which will be beneficial for the industrial applications.

The molecular weights of binder polymers were in the range of 2400 to 8500 g/mol depending on the raw materials used. Some representative gel permeation chromatography (GPC) Mw's of the non-cardo binder polymers are shown in **Figure 5**. The Mw of **BP-1-1**, **BP-1-4**, **BP-2-5**, and **BP-3-2** non-cardo binder polymers were 2431, 4215, 4150 and 8210 g/mol, respectively. The acidic polyester type non-cardo binder polymer **BP-1-1** exhibited low Mw of 2431, since its **CHEP** starting material had low molecular weight and it was not modified with high-molecular-weight monoacid or diol reagents. On the other hand, the other three binder polymers showed much higher Mw's because of the use of relatively high-molecular-weight **SIEP**, **6FB** and **XDO** as diepoxide monomer, monoacid and diol monomer, respectively.

The FT-IR spectra of both **BP-2-5** and **BP-3-2** explicitly showed the existence of ester groups at strong peaks: 1740 cm^{-1} for C=O stretching and 1260 cm^{-1} for C-O stretching (**Figure 6**). Among all signals, the 1137 cm^{-1} and the 843 cm^{-1} referred to C-F and Si-O, respectively. From these FT-IR characterizations, the success of synthesis could be confirmed.

3.2. Photolithographic Evaluations of Binder Polymers

The photolithographic performance of synthesized non-cardo binder polymers were evaluated in comparison of the commercial cardo binder polymer **CBP**. In a typical black photoresist formulation (**Table 2**), 20 wt% of binder polymer and 6 wt% of acidic multifunctional monomer (**PM6**, $f = 6$), both as solutions, were used to provide double bonds for photo-crosslinking reaction. The **MSMA** adhesion promotor (1 wt%) was added to enhance the adhesion of the black PDL

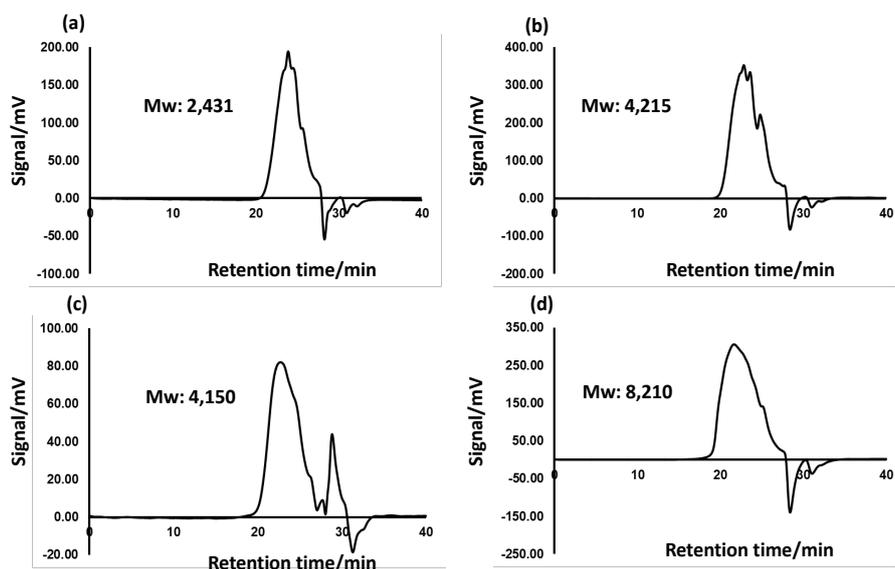


Figure 5. GPC graphs of (a) BP-1-1, (b) BP-1-4, (c) BP-2-5 and (d) BP-3-2 non-cardo binder polymers.

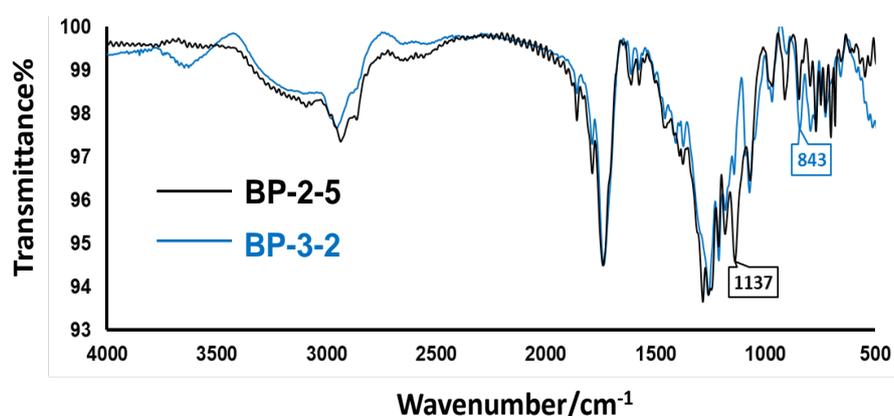


Figure 6. The FT-IR spectra of (a) BP-2-5 and (b) BP-3-2 non-cardo binder polymers.

Table 2. Black photoresist formulations using CBP as cardo binder polymer and other non-cardo binder polymers.

	Photoresist code	PR-0	PR-x-y
Photo-initiator	SPI-03 (Samyang. Co. Ltd.)	6.0	6.0
Photo-sensitizer	Darocure ITX (Ciba, Switz)	2.0	2.0
Binder polymer (45 wt%)	CBP (KISCO, Korea)	20	
Binder polymer (40 wt%)	BP-x-y (BP-1-1~5, BP-2-1~5, BP-3-1~3)		22
Multifunctional monomer	PM6	6.0	6.0
Adhesion promotor	MSMA	1.0	1.0
Solvent	PGMEA	9.0	7.0
Black pigment	BK-4926 (Tokushiki, Japan)	56	56
Total	wt%	100	100

pattern to the silicon wafer substrate by the chemical reaction between the **MSMA** siloxane and hydroxylsilicon on the wafer surface.

In **Table 3**, the **PR-0** black photoresist with the commercial cardo binder polymer (CBP) exhibited good patterning and acceptable level of residue due to the high steric hindrance caused by the bulky fluorene group although the DBD was relatively high (2.22 mmol/g). However, by the same reason, the UV dose required for photo crosslinking reaction was higher than some optimized non-cardo binder polymers because of the reduced space proximity between double bonds.

In the black photoresist with **PR-1-1** through **PR-1-5** as non-cardo binder polymers, the evaluation of PDL patterns and residue after development in the photolithographic process were not as good as the reference **PR-0** although the UV doses for photo cross linking reaction was decreased as shown in **Figure 7**. Among these 5 non-cardo binder polymers, **PR-1-2** and **PR-1-3** behaved the worst since the molecular weight **JEP** and **REP** were quite low, resulting in high DBD of **BP-1-2** and **BP-1-3**. The reason why all these 5 samples behaved poorer

Table 3. List of non-cardo binder polymer properties and photolithographic performances.

(a)						
Performance	PR-0	PR-1-1	PR-1-2	PR-1-3	PR-1-4	PR-1-5
Pattern Evaluation (Good-bad, 1-5)	2	4	5	5	2	3
UV dose (mJ)	120	80	50	60	80	100
DBD (mmol/g)	2.22	2.37	2.38	2.38	2.06	2.15
Residue Evaluation (Good-bad, 1-5)	2	3	4	4	3	3

(b)								
Performance	PR-2-1	PR-2-2	PR-2-3	PR-2-4	PR-2-5	PR-3-1	PR-3-2	PR-3-3
Pattern Evaluation (Good-bad, 1-5)	4	3	3	3	2	3	1	4
UV dose (mJ)	50	80	80	80	80	100	80	60
DBD (mmol/g)	1.18	1.03	1.05	1.08	0.97	1.13	1.10	1.24
Residue Evaluation (Good-bad, 1-5)	4	3	3	3	2	3	1	2

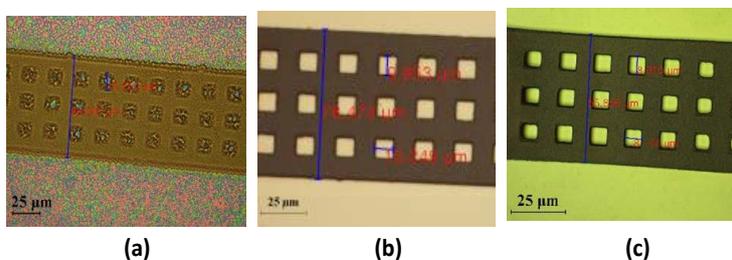


Figure 7. Representative optical microscope images of black PDL patterns obtained with (a) **PR-1-1**, (b) **PR-0** and (c) **PR-3-2**.

than **PR-0** may be attributed to the quite decreased steric hindrance without the fluorene group in the diepoxide monomer, leading to the over-crosslinking reaction upon UV exposure, and thus resulting in irregular pattern and high residue after development. The low level of UV doses may also be due to this effect.

In the **PR-2-1** through **PR-2-5** black photoresists, the DBD values were quite reduced by the introduction of the double-bond-free monoacids in the first step of non-cardo binder polymer syntheses. However, most of the PDL patterning and residue evaluation were still not as good as the **PR-0** reference. These experimental data suggested that the control of photo crosslinking reaction by bulky and rigid fluorene group is more effective than reducing the DBD in the binder polymer, for the purpose of obtaining good patterns of PDL on the OLED panel. Specifically, **PR-2-5** behaved similar with **PR-0**, since the $-CF_3$ groups increased the bulkiness and the compatibility with the other chemical species in the black photoresist.

In the **PR-3-1** through **PR-3-3** black photoresists the DBD values were reduced by the introduction of another diol monomer in the second stage of non-cardo binder polymer synthesis. **PR-3-2** with **BP-3-2** as binder polymer showed the best patterning of PDL and lowest residue after development (**Figure 7**). This seemed to be due to the reduction of DBD in the binder polymer and proper control of steric hindrance in photo crosslinking reaction by adopting bulky and rigid XDO as diol co-monomer in the synthesis as shown in **Figure 3**.

4. Conclusion

In this work, various non-cardo type binder polymers were designed and synthesized to evaluate their performance in comparison to the commercial cardo type binder polymer (**CBP**). Some important results were as following: 1) The commercial **CBP** exhibited both good patterning of PDL and acceptable level of residue after development step in the photolithographic process. This was achieved by the balanced level of double bond density (DBD) and control of photo crosslinking reaction of double bonds by steric hindrance due to the bulky and rigid fluorene group; 2) The reduction of DBD by introducing monoacid or diol co-monomer contributed to the improved patterning of PDL and residue after development; 3) The combination of DBD reduction and increasing the steric hindrance by using bulky and rigid XDO diol co-monomer in non-cardo binder polymer (**BP-3-2**) resulted in both good patterning of PDL and least residue formation after development.

Acknowledgements

This work was supported by the Technology Innovation Program or Industrial Strategic Technology Development Program (10063289, Development of High Temperature Negative tone Photosensitive Black Resin and Fabrication Process for Pol-less AMOLED Devices), funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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