Epoxy Methacrylate Resin as Binder Polymer for Black Negative-Tone Photoresists

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Abstract
Epoxy acrylate (EA) resin, which originates from epoxides, has long been served as a photocurable coating and adhesive material owing to its double bonds. Specifically, alkaline-developable EA resins can be used as a binder polymer in negative-tone photoresists. In this work, we synthesized a series of acidic polyester-type epoxy methacrylate resins, characterized the intermediates and products, and tested their performance as a binder polymer for the photolithographic micro-patterning of the pixel-defining layer on organic light-emitting diodes in comparison to a widely used commercial binder polymer. Copolymer-type binder polymer BP-2-2 was produced excellent patterning with no residue due to its high compatibility with the black mill base.

Keywords
Epoxy Methacrylate Resin, Negative-Tone Photoresist, Binder Polymer

1. Introduction
Epoxy resins, commercialized in the late 1940s, have been used in surface coatings, adhesives, laminates, and other miscellaneous fields [1]. Epoxy acrylate (EA, including epoxy methacrylate) resins can be synthesized by the first reaction of diepoxide with acrylic/methacrylic acid to give double bonds and secondary alcoholic -OH groups, followed by polyesterification between dianhydride and diol units. They excel epoxy resins due to their much faster radiation/thermal curing rate compared to that between curing agents and epoxy resins [2] [3] [4]. Most commercial EA resins are based on epoxy novolacs and bisphenol diglycidyl ethers because of their low cost and easy functionalization.

Apart from the well-known coating and adhesive applications, EA oligomers
with acidic phenolic -OH [5] [6] [7] (Figure 1(a)) or carboxyl (-COOH) groups [8] [9] [10] (Figure 1(b)) have found applications as alkaline-developable binder polymer for negative-tone photoresists. These photoresists have been used for patterning color filter and black matrix [11] of liquid crystal displays (LCDs) as well as the pixel-defining layer (PDL) of organic light-emitting diodes (OLEDs) [12] [13]. Since the acidity of phenolic -OH groups of EAs based on novolac resin is relatively weak, incomplete development may occur, and the introduction of double bonds on the novolac oligomer also requires sacrificial phenolic -OH groups. However, EA resins with polyester linkage, as shown in Figure 1(b), have carboxylic groups as the source of acidity and have better performance in the developmental stage than that with phenolic -OH groups. Moreover, in the case of black photoresists, carboxyl groups can also serve as anchoring groups for the black pigment, enhancing the compatibility among other photoresist components [14].

In this study, we used dicarboxylic acids as starting materials to obtain epoxy methacrylate resin-type binder polymers and evaluated their suitability in the photolithographic process to improve black PDL patterns of OLEDs.

2. Experimental Procedure

2.1. Materials

The binder polymers were synthesized by first reacting dicarboxylic acid with glycidyl methacrylate (GMA) to form diol intermediates with methacrylate groups, followed by the reaction with dianhydrides (with/without external diol as comonomer) to obtain the final binder polymer. The chemical names, code names, and structures of diacids, dianhydrides, and diols used for the syntheses are shown in Table 1. All chemicals were reagent grades and reacted without

![Figure 1](image)  
**Figure 1.** Representative reaction scheme of (a) cresol novolac EA resin and (b) fluorene-based polyester EA resin.
Table 1. List of diacid, dianhydride, diol reactants, and additional selected photoresist components.

| Code Name | Chemical Name                                      | Structure               |
|-----------|---------------------------------------------------|-------------------------|
| **Diacids** |                                                  |                         |
| 6FDC      | 2,2'-Bis(4-carboxyphenyl)hexafluoropropane        | ![Structure](image1)    |
| ODC       | 4,4'-Dicarboxydiaryl Ether                       | ![Structure](image2)    |
| ITCA      | Itaconic Acid                                    | ![Structure](image3)    |
| MLDC      | Methylenebisalicylic Acid (mixture of isomers)    | ![Structure](image4)    |
| 8FDC      | Octafluoroadipic Acid                            | ![Structure](image5)    |
| **Dianhydrides** |                                              |                         |
| 6FDA      | 4,4'-(Hexafluoroisopropylidene)diphthalic Anhydride | ![Structure](image6)    |
| BPDA      | 4,4'-Biphthalic Anhydride (purified by sublimation) | ![Structure](image7)    |
| **Diols** |                                                  |                         |
| XDO       | 3,9-Bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane | ![Structure](image8)    |
| FDO       | 9,9-Bis[4-(2-hydroxyethoxy)phenyl]fluorene        | ![Structure](image9)    |
| SDO       | Bis[4-(2-hydroxyethoxy)phenyl] Sulfone            | ![Structure](image10)   |
| **Other Species** |                                              |                         |
| BHT       | 2,6-Di-tert-butyl-4-methylphenol                 | ![Structure](image11)   |
| TBPB      | Tetrabutylphosphonium Bromide                    | ![Structure](image12)   |
| PM6       | *Acidic Multifunctional Monomer*                 | ![Structure](image13)   |
| MSMA      | 3-(Trimethoxysilyl)propyl Methacrylate           | ![Structure](image14)   |
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further purification. TBPB and MSMA were obtained from Alfa Aesar, PM6 was synthesized by us [10], and the other chemicals were from Tokyo Chemical Industry Co. Ltd. (TCI).

2.2. Synthesis of Homo Binder Polymers: BP-1-x Series

Under nitrogen atmosphere, 5 mmol of 6FDC diacid, 10 mmol of GMA, 0.025 mmol of polymerization inhibitor BHT, 0.05 mmol of catalyst TBPB, and a certain amount of propylene glycol methyl ether acetate (PGMEA) solvent (40 wt% solid) were mixed and stirred at 110°C for 3 h. After cooling, 5 mmol of 6FDA was added with extra PGMEA (40 wt% solid) and continued stirring at 110°C for another 3 h. Up to this point, the reaction mixture appeared as a clear solution. This solution was cooled down and directly used without further work-up (BP-1-1). Binder polymers synthesized with ITCA, ODC, MLDC, and 8FDC as diacids were obtained by the same procedure, and the products were given code names as BP-1-2–BP-1-5, respectively, and those synthesized using 6FDC and BPDA were given BP-1-6 (Figure 2). Specifically, BP-1-3 was insoluble in PGMEA; therefore, it was not tested in the photolithographic evaluation.

2.3. Synthesis of Co-Diol Type Binder Polymers: BP-2-x Series

Under nitrogen atmosphere, 3 mmol of 6FDC, 6 mmol of GMA, 0.015 mmol of inhibitor BHT, 0.05 mmol of catalyst TBPB, and a certain amount of PGMEA solvent (40 wt% solid) were mixed and stirred at 110°C for 3 h to obtain 6FG diol intermediate. After cooling, 2 mmol of external diol XDO and 5 mmol of 6FDA were added with extra PGMEA (40 wt% solid) and continued stirring at 110°C for another 3 h. Up to this point, the reaction mixture appeared as a clear solution. This solution was cooled down and directly used without work-up (BP-2-1). Binder polymers synthesized from FDO and SDO as co-diols were coded as BP-2-2 and BP-2-3 respectively (Figure 3).

**Figure 2.** Synthetic scheme of representative non-cardo binder polymer BP-1-1 to BP-1-6.
2.4. Characterization

The liquid chromatography-mass spectrometry (LC-MS) was recorded using a Bruker 1200 Series & HCT Basic System. The monomer sample in the PGMEA solution was diluted with the eluent (MeOH-H2O system) and directly subjected to the column.

The gel permeation chromatography (GPC) was recorded using an Agilent 1200 S/miniDAWN TREOS. The polymer sample in the PGMEA solution was diluted with THF and directly subjected to the column.

The Fourier-transform infrared spectroscopy (FT-IR) was recorded using a Varian 670 spectrometer. N-hexane was added to the polymer solution, and the precipitate was collected and washed 3 times with n-hexane using centrifugation. The resulting solid was dried under vacuum and subjected to the KBr pellet method.

3. Results and Discussion

3.1. Syntheses and Characterizations of Binder Polymers

Due to the low cost, high diversity, and much higher chemical stability of dicarboxylic acid species compared with diepoxies, we utilized various diacids as starting materials to react with monoepoxide GMA to obtain diepoxy methacrylate-type diol monomers. As shown in Figure 1(b), to get EA diol monomer
from diepoxide as a starting material, acrylic acid increases the cost compared with that synthesized using dicarboxylic acid reacted with glycidyl methacrylate (GMA). Since the reactivity between the epoxide group and the carboxyl group is higher than that between the epoxide group and the secondary -OH group under non-basic catalytic conditions [15], the ring-open polymerization could be suppressed during the formation of diepoxymethacrylate monomers in the presence of TBPB.

To confirm the formation of the 6FG intermediate, its solution starting from 6FDC and GMA (6FG and 6FG', represented as M and M' in the LC-MS graph) was analyzed with LC-MS. Between 16.0 and 16.4 min of retention time, major signals of 6FG ([M + Na]+ and [M − OH]+) and minor signal of [M' − OH]+ were found in which the extraction of hydroxyl radical could be caused by the cleavage of the secondary C-O bond in a glycerol group under the mass spectrometric detector (Figure 4).

The molecular weights of all binder polymers were in the range of 2000 and 4000, in which the copolymers showed a little higher Mw, probably due to the bulkiness of the co-diols XDO, FDO, and SDO (Figure 5). So, each binder polymer or oligomer may have 3 - 5 repeating units on average, providing it with suitable viscosity and reactivity toward cross-linking by free radical polymerization mechanism.

The FT-IR diagrams (Figure 6) of BP-1-1 and BP-2-3 clearly exhibited the C=O stretching of aryl ester groups (1732 cm⁻¹), while the C-F stretching signals (1000 - 1400 cm⁻¹) of BP-1-1 were much higher than those of BP-2-3 due to the higher occupation of 6FDC units of BP-1-1 [16].

3.2. Photolithographic Evaluation of Binder Polymers

The photolithographic performance of the synthesized epoxy methacrylate binder polymers was evaluated in comparison to the commercial cardo binder polymer CBP, whose structure is shown in Figure 1(b). In a typical black photoresist formulation (Table 2), 22 wt% binder polymer and 6 wt% acidic multifunctional monomer (PM6, f = 6) were used to provide double bonds for the photo-crosslinking reaction. The MSMA adhesion promoter (1 wt%) was added to enhance the adhesion of the black PDL pattern to the silicon wafer substrate by the chemical reaction between the MSMA siloxane and hydroxyl silicon on the wafer surface. In this work, the UV dose was fixed as 60 mJ/cm².

Figure 4. LC-MS graph of 6FG at 16.0-16.4 min of retention time.
Figure 5. GPC graphs of selective binder polymers: (a) BP-1-1, (b) BP-1-6, (c) BP-2-1, and (d) BP-2-2 binder polymers.

Figure 6. FT-IR diagrams of selective binder polymers: BP-1-1 and BP-2-3.

Table 2. Black photoresist formulations using CBP as standard binder polymer and other epoxy acrylate binder polymers.

| Photoresist code | PR-0 | PR-x-y |
|------------------|------|--------|
| Photo-initiator  | SPI-03 (Samyang. Co. Ltd.) | 4.0 | 4.0 |
| Photo-sensitizer | Darocure ITX (Ciba, Switz) | 1.0 | 1.0 |
| Binder polymer (45 wt%) | CBP (KISCO, Korea) | 20 | |
| Binder polymer (40 wt%) | BP-x-y (BP-1-1–6, BP-2-1–3) | 22 | |
| Multifunctional monomer (50 wt%) | PM6 | 6.0 | 6.0 |
| Adhesion promotor | MSMA | 1.0 | 1.0 |
| Solvent | PGMEA | 12 | 10 |
| Black pigment | BK-4926 (Tokushiki, Japan) | 56 | 56 |
| Total | wt% | 100 | 100 |
The black photoresist with CBP binder polymer (PR-0) gave better pattern and residue level (Table 3) under 60 mJ/cm² of UV dose and 4 wt% photo-initiator compared with our previous studies [9] [10]. Among the 5 soluble homopolymer candidates, BP-1-2 and BP-1-4 caused issues during development with aqueous alkaline, presumably due to the high double bond density (mmol of double bonds in 1 g of sample, DBD) and high adhesion to the substrate, respectively. When the linear diacid 8FDC was used as the starting material, the photo-patterning and residue became better (PR-1-5) due to the higher number of -CF₃ groups in the binder polymer, which enhanced the compatibility with the black mill base. However, the black photoresist (PR-1-1) with BP-1-1 as the binder polymer exhibited better performance in the photolithographic evaluation (Figure 7(b)) than PR-0 (Figure 7(a)) since the binder polymer BP-1-1 had -CF₃ groups in both diacid (6FDC) and dianhydride (6FDA). The performance of PR-1-6 was not as good as PR-1-1, probably due to the lack of -CF₃ groups in BPDA dianhydride instead of 6FDA.

To further reduce the residue on the substrate after development, we utilized 3 comonomer diols, as shown in Figure 3 to synthesize copolymer-type binder polymers (PR-2-1, PR-2-2, PR-2-3). Among the three copolymer-type binder polymers, the binder polymer BP-2-2 gave the best photolithographic patterning, as shown in Table 4 and Figure 7(d). The BP-2-1 binder polymer made with XDO comonomer showed slightly over-crosslinked pattern (Figure 7(c)), while the BP-2-3 binder polymer gave no pattern. This could be explained by the steric effect of co-diols: FDO offers planar fluorene structure outside the polymer chain, which could more effectively interact with the black mill base, and good compatibility with -CF₃ groups.

Table 3. List of epoxy methacrylate binder polymer properties and photolithographic performances.

| Performance        | PR-0 | PR-1-1 | PR-1-2 | PR-1-4 | PR-1-5 | PR-1-6 |
|--------------------|------|--------|--------|--------|--------|--------|
| Binder polymer     | CBP  | BP-1-1 | BP-1-2 | BP-1-4 | BP-1-5 | BP-1-6 |
| Monomers           |      |        |        |        |        |        |
| Diacid             |       |        |        |        |        |        |
| dianhydride        |       |        |        |        |        |        |
| Pattern Evaluation | (Good-bad, 1-5) | 2  | 1  | 4  | 4  | 3  | 3  |
| DBD (mmol/g)       | 2.22  | 1.81  | 3.56  | 1.94  | 1.99  | 2.09  |
| Residue Evaluation | (Good-bad, 1-5) | 2  | 2  | 5  | 5  | 3  | 3  |

¹: The pattern shapes and sizes are almost the same as those of the photomask. 2: The pattern shapes are almost the same as those of the photomask, but the sizes are within 90% error. 3: The pattern shapes appear a little distorted or wavy. 4: The patterns lost thickness or are incomplete. 5: There are almost no patterns at all. ²: The developed parts are trace-free and appear like new wafer under OM. 2: The developed parts show traces under OM. 3: The developed parts show traces to the naked eye. 4: The developed parts show obvious residues to the naked eye. 5: Incomplete development.
Table 4. List of black photoresists containing copolymer-type binder polymer and their photolithographic performances.

| Performance          | PR-0 | PR-2-1 | PR-2-2 | PR-2-3 |
|----------------------|------|--------|--------|--------|
| Binder polymer       | CPB  | BP-2-1 | BP-2-2 | BP-2-3 |
| Co-monomer diols     | XDO  | FDO    | SDO    |        |
| Pattern Evaluation   | 2    | 3      | 1      | 3      |
| (Good-bad, 1-5)      |      |        |        |        |
| DBD (mmol/g)         | 2.22 | 1.08   | 0.999  | 1.06   |
| Residue Evaluation   | 2    | 2      | 1      | 3      |
| (Good-bad, 1-5)      |      |        |        |        |

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

4. Conclusion

In this work, a series of epoxy methacrylate-type binder polymers were synthesized using dicarboxylic acids as starting materials. The photo-initiator loading, UV dose, and DBD of binder polymers contributed to the photolithographic cross-linking reaction simultaneously; therefore, we tuned these parameters carefully to optimize cross-linking. Moreover, -CF3 groups and bulky fluorene groups were found to improve the compatibility with the black mill base, resulting in less residue on the wafer after the development. The black photoresist PR-2-2 with the copolymer-type binder polymer BP-2-2 produced the optimal PDL pattern with the least residue in the photolithographic tests. This work can pave the way for the design of binder polymers for negative-tone black photoresist and the optimization of photolithographic process conditions.

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Conflicts of Interest

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