

# Synthesis of UV-Curable/Alkali-Soluble Dispersants Used for Black Photoresist with a High Loading of Carbon Black

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**ABSTRACT:** This research synthesized a functional dispersant, not only providing a good dispersion of carbon black (CB) but also possessing ultraviolet (UV)-curable and alkali-soluble properties, by a two-step process. Firstly, bisphenol-A epoxy diacrylate was reacted with benzophenone tetracarboxylic dianhydride at different molar ratios to obtain UV-curable/alkali-soluble resins. In the second step, these resins would possess dispersion ability of CB by reaction with an isocyanate-containing methacrylate. The prepared dispersants were evaluated by their dispersion ability and the light absorption property of CB. The results showed that one of the dispersants was able to disperse CB in the solvent up to 10 wt % with a mean particle size about 100 nm. This particu-

lar dispersant had a moderate amount of amino-containing groups (such as urethane, amide, and imide) serving as anchoring sites on CB, and a sufficiently long chain ( $M_n \sim 2600$ ) to provide a steric repulsion among CB particles. The advantage of this CB/dispersant system is that no other curable resins are needed. By using a suitable photoinitiator, the present CB/dispersant system could reach a polymerization rate of  $1.05 \times 10^{-3} \text{ (s}^{-1}\text{)}$ , and a black pattern of 10  $\mu\text{m}$  in width on a glass substrate was obtained through an UV-lithography process. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1803–1813, 2010

**Key words:** carbon black; dispersions; photoresists

## INTRODUCTION

Carbon black (CB) is an important pigment that has been widely used in ink, tinting, and toner applications.<sup>1–4</sup> For practical use, a stable CB dispersion in organic or water solution is important because CB particles are prone to aggregation.<sup>5,6</sup> In some specific fields, a high loading of CB dispersion in solvent up to 10 wt % is desired in order to be applied in light-shielding applications. For example, in the application of display devices, such as black pattern or black matrix of color-filter in liquid crystal display and plasma display,<sup>7,8–10</sup> a black photoresist is generally prepared by mixing CB, a dispersant, an alkali-soluble resin, a multifunctional monomer, a photoinitiator (PI), and solvent with a weight percentage of 8–12, 1–2, 4–8, 1–2, 1–2, and 75–85%, respectively. The dispersant is used to provide the stability of CB in dispersion for a long storage time. Unfortunately, the preparation of a stable CB dispersion with fine particles is not easy; and in many cases, it is prepared by using a surfactant or dispersant.<sup>5,7,11–15</sup> For example, Wang et al.<sup>13</sup> reported a dispersant used in water medium, namely, poly-

(ethylene oxide)-*b*-poly(2-dimethylamino ethyl methacrylate). It has a tertiary amine group serving as an anchoring site and a long poly(ethylene oxide) chain for a steric repulsion. Kamata et al.<sup>7</sup> synthesized a polyacrylate dispersant having the tertiary amine group as well as its quaternarized derivative. The influence of composition of the prepared polyacrylate dispersant on the dispersion ability of CB in an organic solvent (propylene glycol monomethyl ether acetate, PGMEA) was also evaluated. Recently, it has been reported that through the surface modification of CB by polymers via a chemical or physical method, a good dispersion of CB in solvent could also be achieved.<sup>2,13,16–21</sup> The alkali-soluble resin generally contains double bonds that can be cured under ultraviolet (UV)-irradiation in which the portion that is not irradiated can be dissolved and washed away in an alkaline solution. This type of resin is called negative-tone photoresist. It therefore can form a pattern through an UV lithography technology. A variety of UV-curable and alkali-soluble resins have been developed.<sup>7,10,22–24</sup> Kamata et al.<sup>7</sup> used a free radical polymerization to prepare an alkali-soluble copolymer, poly(methacrylate acid-methyl methacrylate-benzyl methacrylate-2-hydroxyethyl methacrylate). Afterwards, the alkali-soluble copolymer was grafted with 2-methacryloyloxyethyl isocyanate to possess the UV-curable property. Lee<sup>10</sup>

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prepared UV-curable/alkali-soluble resins by polycondensation between bisphenolfluorene-based epoxy acrylate and tetracarboxylic dianhydride at different molar ratios. Subsequently, the influences of composition on the resolution and photosensitivity of pattern were investigated. Nishikubo and coworkers<sup>24</sup> synthesized a hyperbranched polyimide containing both methacrylate and carboxylic acid groups at the chain ends through the reaction between carboxylic acid anhydrides, trisamines, and glycidyl methacrylate.

In this study, we have synthesized a CB dispersant which can not only disperse a high loading of CB, but is also UV-curable and alkali-soluble. This kind of dispersant thus can be directly used as a black photoresist. A two-step reaction was adopted to synthesize the UV-curable/alkali-soluble dispersant. UV-curable/alkali-soluble resins were first synthesized by condensation between the OH group of bisphenol-A epoxy diacrylate (EPA) and the anhydride group of benzophenone tetracarboxylic dianhydride (BTDA) at different molar ratios. In the second step, these resins were given the ability to disperse CB by reaction with an isocyanate-containing methacrylate monomer. The reaction route is shown in Figure 1. Furthermore, to prepare successful CB photoresists, different PIs were evaluated and compared. Since CB is a light-shielding material and also a good radical scavenger, the selection of PI is very important. Finally, stable CB dispersions with different compositions were prepared through a ball-milling process, and black patterns thus formed on a glass substrate by UV-lithography were then evaluated.

## EXPERIMENTAL

### Material

2-Hydroxyethyl methacrylate (HEMA, ACROS) was free from moisture under reduced pressure prior to use. Bisphenol-A epoxy diacrylate (EPA, AGI Corporation), benzophenone tetracarboxylic dianhydride (BTDA, ACROS), isophorone diisocyanate (IPDI, Lancaster), di-n-butyltin dilaurate (DBTDL, TCI), propylene glycol monomethyl ether acetate (PGMEA, Grand Chemical), tetrahydrofuran (THF, ACROS), potassium hydroxide (KOH, ACROS), sodium hydroxide (NaOH, SHIMAKYU), sodium hydrogen carbonate (NaHCO<sub>3</sub>, SHIMAKYU), and CB (Regal 400R, CABOT Co., Ltd) were all used as received without further purification. The CB was found to have carboxylic acid group on the surface. 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazole-3-yl]-1-(O-acetyl oxime) (I242, Ciba), 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholino)-propan-2-one (I907, Ciba), 2-benzyl-2-dimethylamino-1-(4-morpholino-

phenyl)-butan-1-one (I369, Ciba), and 2,4,6-trimethyl benzoyldiphenyl phosphine oxide (TPO, BASF) were used as photoinitiators.

### Synthesis of UV-curable/alkali-soluble resins, A1 and A2

EPA and BTDA were dissolved in PGMEA with a total concentration of ca. 40 wt %. The solution was stirred with a magnetic stirring bar and kept at 100°C for 12 h in a nitrogen atmosphere to synthesize two UV-curable/alkali-soluble resins, A1 and A2 (cf. Fig. 1). Molecular weight and functional group concentration of A1 and A2 were measured and are listed in Table I.

### Synthesis of UV-curable/alkali-soluble dispersants, B1 and B2

In order to have the dispersion ability of CB in addition to the UV-curable and alkali-soluble properties, the synthesized resins, A1 and A2, were further reacted with an isocyanate-containing methacrylate monomer (H-I) to become B1 and B2, respectively (see Fig. 1). The H-I monomer containing both isocyanate functional group and methacrylate double bond was synthesized by reaction of equal amounts of HEMA and IPDI (corresponding to [OH]/[NCO] = 1/2) in PGMEA solvent and catalyzed by DBTDL. The reaction to synthesize H-I monomer was conducted in an ice bath under a nitrogen atmosphere for 1 h. The detailed reaction and its product characterization were described elsewhere.<sup>25</sup> Afterwards, a proper amount of A1 or A2 solution was added to the above H-I solution in which the solid content in PGMEA was maintained at 40 wt %. The temperature was raised and kept at 85°C, and the reaction mixture was monitored by Fourier transform infrared spectroscopy (FTIR, DIGILAB FTS4000). The reaction product, B1 or B2, was finally obtained when the absorbance indicated that the isocyanate group was consumed completely. Molecular weight and functional group concentration of B1 and B2 were measured and are listed in Table I.

### Structural analysis

Structures, especially functional groups of A1, A2, B1, and B2 were characterized by FTIR in the range of 4000–900 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup>. Sample solution was cast on CaF<sub>2</sub> and the solvent was evaporated. Absorbance mode was used to obtain FTIR spectra. The molecular weight of various products was determined by gel permeation chromatography (GPC) using a pump (ABI, spectroflow 400) equipped with three columns (Waters), and a RI detector (Shodex RI-71) under the effluent of THF

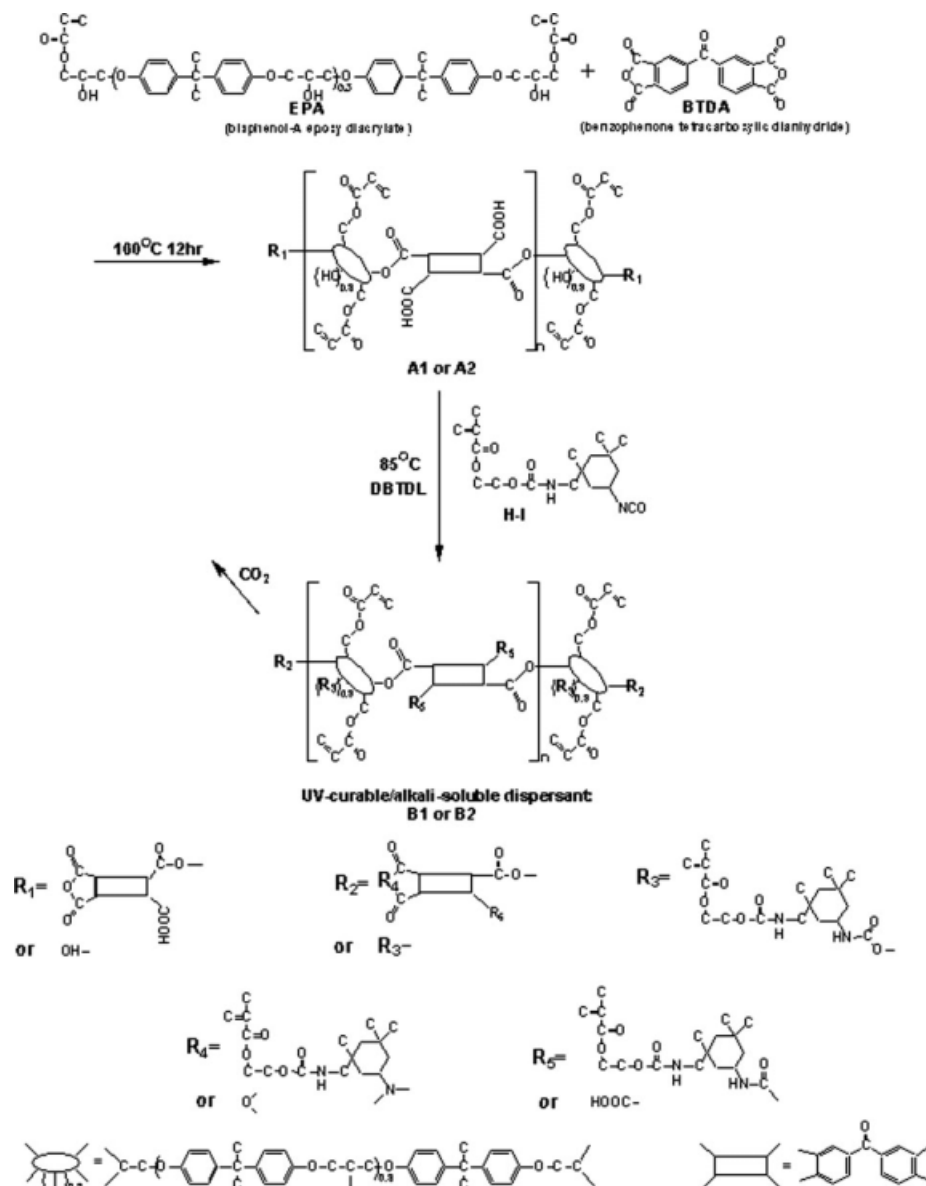


Figure 1 Synthesis and proposed structure of A1, A2, B1, and B2.

TABLE I  
Molecular Weight and Various Functional Group Concentrations of A1, A2, B1, and B2

Sample	A1	A2	B1	B2
Component	EPA/BTDA	EPA/BTDA	EPA/BTDA/H-I	EPA/BTDA/H-I
Molar ratio	1/2	5/4	1/2/2	5/4/2.67
$M_n/M_w^a$	1130/3450	2390/7670	1600/4010	2590/10600
Carboxylic acid (mol/g) <sup>b</sup>	$5.1 \times 10^{-3}$	$2.3 \times 10^{-3}$	$2.2 \times 10^{-3}$	$1.5 \times 10^{-3}$
Acrylate (mole/g)	$1.7 \times 10^{-3}$	$2.6 \times 10^{-3}$	$1.1 \times 10^{-3}$	$2.1 \times 10^{-3}$
Methacrylate (mole/g)	0	0	$1.1 \times 10^{-3}$	$0.6 \times 10^{-3}$
Amino group (mol/g) <sup>c</sup>	0	0	Imide: $0.7 \times 10^{-3}$ NH: $1.6 \times 10^{-3}$	Imide: $0.2 \times 10^{-3}$ NH: $0.9 \times 10^{-3}$
Aromatic group (mol/g)	$5.7 \times 10^{-3}$	$5.5 \times 10^{-3}$	$3.7 \times 10^{-3}$	$4.5 \times 10^{-3}$
Total amount of anchoring groups (mol/g) <sup>d</sup>	$5.7 \times 10^{-3}$	$5.5 \times 10^{-3}$	$6.0 \times 10^{-3}$	$5.6 \times 10^{-3}$

<sup>a</sup> Molecular weight was measured by GPC.

<sup>b</sup> Carboxylic acid concentration was determined by using a titration method.

<sup>c</sup> The concentrations of imide group in B1 and B2 were calculated from FTIR spectra.

<sup>d</sup> The sum of amino-containing groups and aromatic ring.

solvent at a flow rate of 1 mL/min. The reported values of molecular weight were based on the polystyrene standards. The concentrations of carboxylic acid group in A1, A2, B1, and B2 were measured with a titration method using potassium hydroxide solution as the standard. The pH value during the titration process was monitored by using a pH meter (HORIBA F-51).

### Evaluation of dispersion ability of carbon black

Various CB dispersions in PGMEA were prepared by using a ball-milling process. Specifically, 2.5 g of a resin solution (40% of A1, A2, B1, or B2 in PGMEA) was added with 1 g of CB, additional 6.5 g of PGMEA, and 15 g of zirconium oxide bead with a diameter of 2 mm. The weight ratio of CB to resin was thus 5/5 (wt/wt). The mixture was sealed into a vial and rolled in the ball miller (Shin Kwang MUBM-340) at a speed of 500 rpm for 1 day. Particle size and morphology of CB were evaluated with a dynamic light scattering analyzer (DLS, MALVERN, Zetasizer 3000HS) and a scanning electron microscope (SEM, Hitachi S-2400), respectively.

### UV/visible absorption spectra of CB dispersions and PIs

The absorption spectra of CB dispersions using B2 as the dispersant were recorded with an UV/Visible spectrophotometer (Thermo-Spectronic HELIOS). Five CB/B2 dispersions (5/5, 5/4, 5/3, 5/2, 5/1 in wt ratio) in PGMEA were prepared. The concentration of CB in PGMEA was 0.001%. The sample in a quartz cell with a path length of 1 cm was subjected to UV/Visible light between 250 and 700 nm. The data interval was 1.0 nm. In addition, the absorption spectra of different PIs were also recorded.

### Photopolymerization of dispersant/CB composite

Photosensitivity of dispersant/CB composites with different PIs was studied with a photodifferential scanning calorimeter (photo-DSC, Perkin-Elmer Diamond DSC coupled with EXFO OmniCure Series 2000). Samples were prepared by adding specific amounts of B2 (10 wt%), PI (0.1 wt %), with or without CB (0.1 wt %) into the PGMEA solvent. Approximately 30 mg of the above solution was dropped into an aluminum pan with a micropipette. It was then dried at 50°C for 1 h, removed to the photo-DSC, covered with a quartz glass, and finally equilibrated at 50°C for 10 min. Polymerization was initiated by UV irradiation in a nitrogen atmosphere, and the reaction heat was monitored. The wavelength range of UV light was 250–450 nm.

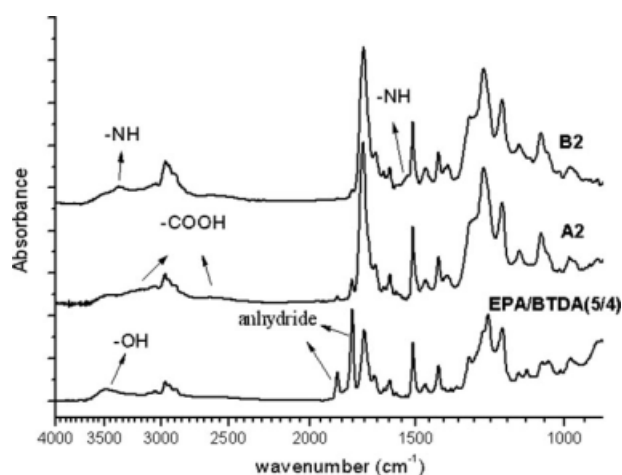
### Pattern formation from UV lithography

Black photoresist was prepared by dissolving a specific amount of I242 initiator (ca. 2 wt %) into the CB dispersion and then dropped onto a glass substrate. A black film was then obtained from a spin coating process with 900 rpm for 10 s. The film was pre-baked at 50°C for 2 min and subsequently exposed to UV light (200 mJ/cm<sup>2</sup>) with a direct contact between the 10 μm-stripe photomask and the black film. The black pattern was developed in an alkaline developer (NaHCO<sub>3</sub>/NaOH = 5 g/1.5 g in 200 mL water). The resulting pattern was postbaked at 200°C for 30 min, and finally inspected by using an optical microscope (OM, Olympus MX 40) as well as a SEM (Hitachi S-2400).

## RESULTS AND DISCUSSION

### Synthesis of UV-curable/alkali-soluble resins, A1 and A2

In this work, UV-curable/alkali-soluble resins, A1 and A2, were first prepared by esterification between OH groups of EPA and anhydride groups of BTDA at different molar ratios (see Fig. 1). Their structures were confirmed by FTIR and GPC analysis. Table I lists the feeding molar ratios of EPA to BTDA and all calculated functional group concentrations in the A1 and A2 products. Taking A2 for an example, it was produced from the reaction between EPA and BTDA with a molar ratio of 5 to 4. Figure 2 shows FTIR spectra of EPA/BTDA mixture (5/4) before reaction and its reaction product A2. It can be seen in the spectrum of A2 that the absorbance of hydroxyl group between 3200 and 3600 cm<sup>-1</sup> originally present in EPA largely decreases due to the reaction with the anhydride group of BTDA. This reaction results in the formation of



**Figure 2** FTIR spectra of EPA/BTDA mixture, A2, and B2.



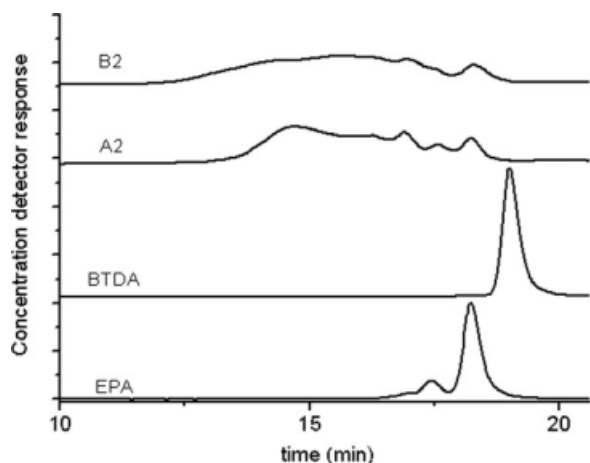


Figure 3 GPC curves of EPA, BTDA, A2, and B2.

carboxylic acid group which exhibits a broad absorption peak between 2500 and 3300  $\text{cm}^{-1}$ . Yet, small peaks at 3500, 1855, and 1780  $\text{cm}^{-1}$  are still observed, indicating the existence of some unreacted hydroxyl and anhydride groups in A2.

The formation of A2 is also confirmed by GPC as shown in Figure 3. First, it can be seen that the original EPA reactant has two peaks, indicating that there are two different molecular weights in EPA, i.e.,  $n = 0$  and 1 (see Fig. 1). After reaction, Figure 3 shows that these two peaks almost disappear due to the reaction with BTDA. Also the original BTDA peak disappears completely in the chromatogram of A2 product. A broad multipeak with higher molecular weights is thus observed for the A2 product.

#### Synthesis of UV-curable/alkali-soluble dispersants, B1 and B2

As mentioned in the Introduction, the amino-containing groups are effective as anchoring sites for CB.<sup>7,13,25</sup> Therefore, to introduce amino-containing groups, an H-I monomer was thus synthesized and added to react with A1 and A2 to produce B1 and B2, respectively, as effective dispersants. The structure of H-I monomer is shown in Figure 1, in which it has an isocyanate functional group and methacrylate double bond. Therefore, the reaction with H-I monomer not only can introduce amino-containing functional groups but also increase the concentration of double bonds which can promote the rate of polymerization and the crosslinking density when exposed to UV radiation. Taking B2 for an example, it was synthesized by reaction of H-I monomer with A2. The isocyanate group in H-I reacted with the hydroxyl, carboxylic acid, and anhydride group of A2, thus producing urethane, amide, and imide groups, respectively, in the B2 product. The reaction was conducted at 85°C and monitored by FTIR until the isocyanate group in H-I monomer was con-

sumed completely. During the reaction, gas bubbles of  $\text{CO}_2$  were observed due to the reaction between the isocyanate group and the carboxylic acid group as well as with the anhydride group.

The FTIR spectrum of B2 is also shown in Figure 2. Compared to A2, the peak originally in A2 at 3500  $\text{cm}^{-1}$  almost disappears indicating that the hydroxyl group of A2 was completely reacted with the isocyanate group of H-I. The concentration of carboxylic acid measured with a titration method decreases from  $2.3 \times 10^{-3}$  mol/g for A2 to  $1.5 \times 10^{-3}$  mol/g for B2 due to the reaction with the H-I. New peaks at 3375 and 1540  $\text{cm}^{-1}$  are found and assigned to the NH stretching and bending vibration of urethane and amide groups. Besides, the original anhydride group in A2 as indicated at 1780 and 1855  $\text{cm}^{-1}$  almost disappears due to the reaction with the isocyanate group in H-I. Therefore, from the above evidence, it can be deduced that the B2 product has amino-containing groups such as urethane, amide, and imide groups. The presumed structure of B2 is shown in Figure 1 and its various functional group concentrations are listed in Table I. The molecular weight of B2 measured by GPC (cf. Fig. 3) is found to be a little higher than that of A2 due to the introduction of H-I into B2.

#### Influence of different dispersants on the particle size of CB

CB is an important pigment which has been widely used in many applications. However, CB particles are prone to aggregation because of high specific area and oil absorption ability.<sup>5,6</sup> The selection of dispersant is thus essential to prepare a stable CB dispersion, especially for a high loading of CB. Two structural factors are thought to be important: (1) a sufficiently long chain to provide steric repulsion,

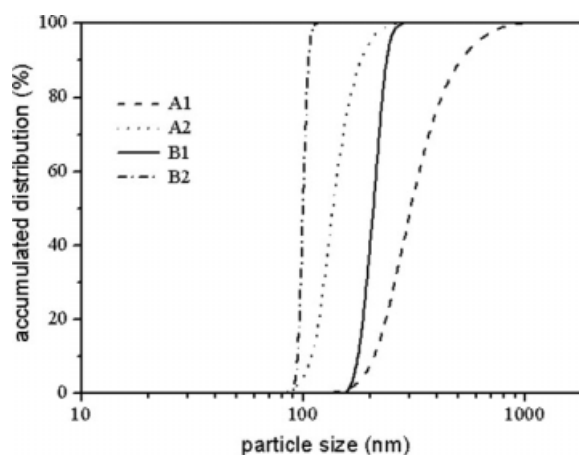
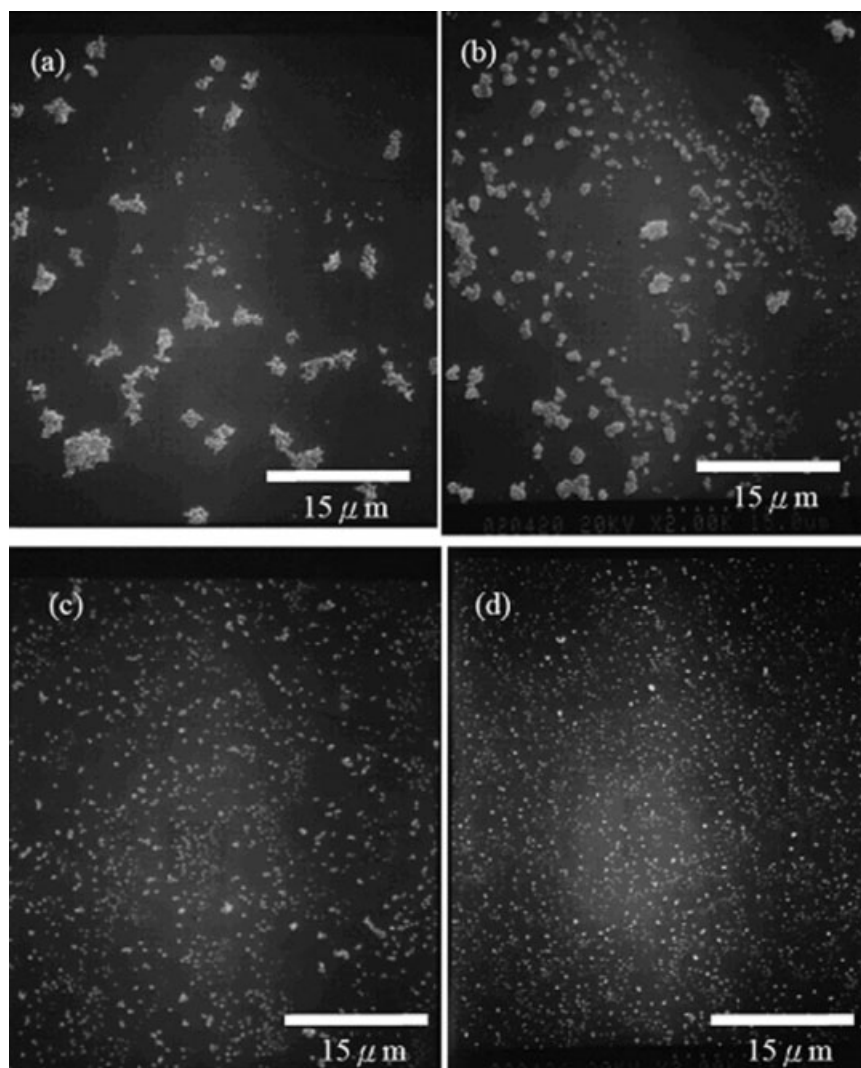


Figure 4 Influence of A1, A2, B1, and B2 resin on the particle size of CB determined by DLS. The weight ratio of CB to resin was 5/5 (wt/wt).

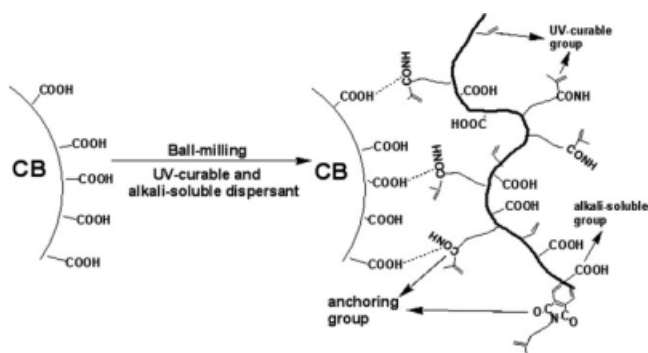


**Figure 5** SEM pictures of CB dispersed by (a) A1, (b) B1, (c) A2, (d) B2 resin. The weight ratio of CB to resin was 5/5 (wt/wt).

(2) an anchoring group that can interact with the surface of CB particles, for example, an amino-containing group or hydroxyl group capable of interacting with the surface carboxylic acid of CB through hydrogen bonding,<sup>26,27</sup> or an aromatic ring to provide  $\pi$ - $\pi$  stacking interaction with CB graphene surface.<sup>27-30</sup> In this work, A1, A2, B1, and B2 with different molecular structures were all tried to prepare CB dispersions, and their particle size and morphology were evaluated by both DLS and SEM techniques. The concentrations of CB and resin were both maintained at 10 wt % in the PGMEA solvent for preparing the dispersion (the weight ratio of CB to resin was 5/5). The influence of anchoring group on the particle size of CB is discussed by comparing structures of A1 and B1. As listed in Table I, the molecular weights and the total amounts of anchoring group between A1 and B1 are similar, but the particle size of CB dispersed by B1 is smaller than that by A1 as shown in Figures 4 and 5(a,b). This is

explained by their possession of different anchoring groups. B1 contains urethane, amide, and imide functional groups, which can serve as better anchoring groups due to the formation of hydrogen bonds with the carboxylic acid group on the surface of CB. However, A1 has only aromatic groups to provide  $\pi$ - $\pi$  stacking interaction which is not as strong as the hydrogen bonding. Hence, poor dispersion or stability of CB by A1 is observed. A similar behavior is observed in Figure 4; the particle size of CB dispersed by B2 is smaller than that by A2 for the same reason.

The effect of molecular weight of dispersant on the particle size of CB is discussed by comparing B1 and B2. Their total amounts of anchoring groups are almost the same, but a smaller particle size of CB by B2 is observed as shown in Figures 4 and 5(b,d). Since the molecular weight of B2 ( $M_n \sim 2600$ ) is larger than that of B1 ( $M_n \sim 1600$ ), the larger molecular weight of B2 can provide more steric hindrance



**Figure 6** A cartoon shows the interactions between the UV-curable/alkali-soluble dispersant and CB.

to protect CB from aggregation. The importance of a sufficiently long chain for steric repulsion is noticed again by discovering that the particle size of CB dispersed by A2 ( $M_n \sim 2400$ ) is smaller than that by B1 ( $M_n \sim 1600$ ), although B1 contains more effective anchoring groups. Therefore, it is concluded that the molecular weight of dispersant should be high enough to provide sufficient steric repulsion in order to have a good dispersion of CB. On the contrary, when molecular weight is not high enough, the dispersant ability could be limited even though the dispersant has effective anchoring groups.

In comparison, the smallest particle size of CB, ca. 100 nm, is achieved by using the B2 dispersant. It has a sufficiently long chain to provide steric hindrance and several effective anchoring groups to prevent CB particles from aggregation. A cartoon describing the interactions between the UV-curable/alkali-soluble dispersant with CB is shown in Figure 6. Therefore, the B2 dispersant was used to prepare a stable CB dispersion in PGMEA for the following studies.

### Effect of CB particle size on light absorption property

CB photoresist with a high light-absorption property is desired to be a good light-shielding material. It is known that the blackness of CB is normally a function of particle size, especially for finer CB particles.<sup>9</sup> In this work, five CB dispersions with different particle sizes were prepared by using different weight ratios of CB/B2: 5/5, 5/4, 5/3, 5/2, and 5/1 (wt/wt), and the extent of light absorbed by CB dispersion was determined with an UV/Visible spectrophotometer as shown in Figure 7. Apparently, the particle size of CB increases by decreasing the B2 composition. With the smallest particle size (ca. 104 nm), the CB dispersion shows the highest absorption of light. On the contrary, poor light absorption is observed when the particle size of CB is large. This is because under the same weight, the smaller the

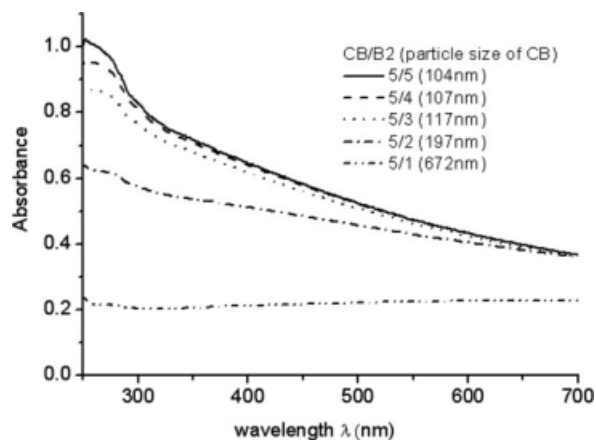
particle size is, the larger is the total surface area. For instance, at the wavelength of 400 nm, the absorbance of CB dispersion with a particle size of 104 nm is about 0.65; however, the value decreases to about 0.20 when the particle size is about 672 nm. As a result, the CB dispersion with a CB/B2 = 5/5 giving a particle size of about 104 nm is suitable to be an effective light-shielding material.

### Selection of photoinitiator for preparing CB/B2 photoresist

As mentioned earlier, CB is a light-shielding material. Therefore, the fraction of light absorbed by PI in the black photoresist would be reduced. Furthermore, the radicals produced by PI are easily trapped by CB which is also a good radical scavenger. Consequently, the effective radicals generated by PI are reduced.<sup>8,16–19,31,32</sup> It is thus expected that the rate of photoinitiated polymerization of CB/B2 would be very small during the preparation of the black pattern through an UV-lithography technology. In view of this aspect, the selection of PI is extremely important. In this study, four kinds of PIs, I242, I369, I907, and TPO, were evaluated and compared because they are highly reactive and widely used in the pigment-curing system.<sup>33–35</sup> These PIs are all classified as Norrish-Type I PIs, which undergo a direct photocleavage reaction to produce primary radicals capable of inducing polymerization when exposed to UV light.

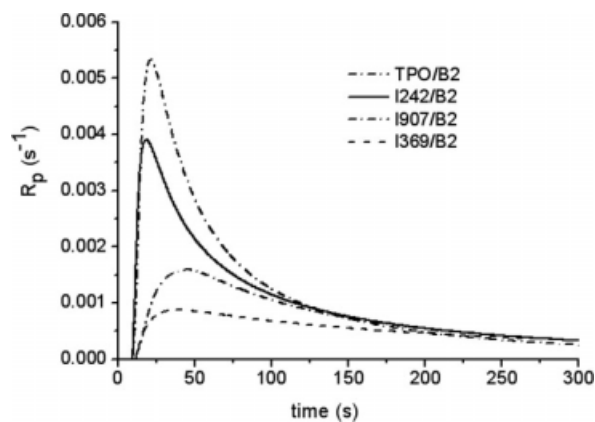
### Influence of photoinitiator on the rate of polymerization of B2 without CB

The effect of different PIs on the rate of polymerization of B2 was first examined by using a photo-DSC in the absence of CB. Because the photopolymerization



**Figure 7** UV/Visible spectra of CB dispersions with different weight ratios of CB/B2: 5/5, 5/4, 5/3, 5/2 and 5/1 (wt/wt) in the PGMEA solvent. The concentration of CB in PGMEA was 0.001 wt %.





**Figure 8** The effect of different PIs on polymerization rate of B2 at 50°C in the absence of CB in a nitrogen atmosphere. The polymerization rate was measured by photo-DSC and the UV light intensity is 1.3 mW/cm<sup>2</sup>.

reaction is exothermic, the rate of polymerization can be monitored by measuring the heat flow during irradiation. The heat generated during polymerization is attributed to the reaction of acrylate and methacrylate double bonds present in B2. However, the heat of reaction from acrylate and methacrylate cannot be separated in the photo-DSC experiment; therefore, the rate of polymerization is assumed to be an average consumption rate of double bonds in acrylate and methacrylate. The results are shown in Figure 8. The  $R_{p,max}$  (maximum rate of polymerization corresponding to the peak value) of B2 decreases in the order of TPO > I242 > I907 > I369. This decreasing order can be explained from the reaction mechanism of radical generation. The photocleavage of TPO produces benzoyl and phosphonyl radicals upon irradiation of UV light as shown in Figure 9(a). I369 also produces two radicals,  $\alpha$ -aminoalkyl radical and benzoyl radical, with a tertiary morpholine nitrogen atom, owing to the  $\alpha$ -cleavage process upon absorption of UV light [Fig. 9(b)]. However,  $R_p$  of B2 initiated by I369 is much smaller than that by TPO. This is explained from the occurrence of ionic complex<sup>13,21</sup> between carboxylic acid of B2 and the primary radical having tertiary amine group generated from I369. This strong interaction thus reduces the mobility and efficiency of the primary radical. Compared with I369, the primary radicals generated from TPO do not have any tertiary amine groups; therefore, no interactions between radicals from TPO and carboxylic acid of B2 are formed and the mobile radicals are capable of inducing a fast rate of polymerization. This deduction is further confirmed by using another resin, A1, which has a higher concentration of carboxylic acid than B2. The  $R_p$  of A1 initiated by I369 was measured (data not shown here) and found to be further decreased when compared with the B2/I369 system.

As illustrated in Figure 8, compared with I369, a little higher  $R_p$  of B2 by I907 is observed because one of the primary radical, benzoyl radical with a methylthiol group, is mobile to induce a higher polymerization rate [cf. Fig. 9(c)]. Unfortunately, another primary radical,  $\alpha$ -aminoalkyl radical, is inefficient because its mobility is restricted due to the formation of ionic complex. According to the reason mentioned earlier, it is concluded that I907 and I369 are not suitable for initiating the polymerization of resins containing the carboxylic acid group. Interestingly, the  $R_{p,max}$  of B2 initiated by I242 is 2.5–4 times as large as that initiated by I907 or I369 (Fig. 8), although the iminyl radical from I242 also contains the tertiary amine group. It is probably because the other radical from I242, methyl radical, is so small that it is highly mobile in the viscous resin matrix and thus highly reactive for initiating radical polymerization [see Fig. 9(d)].

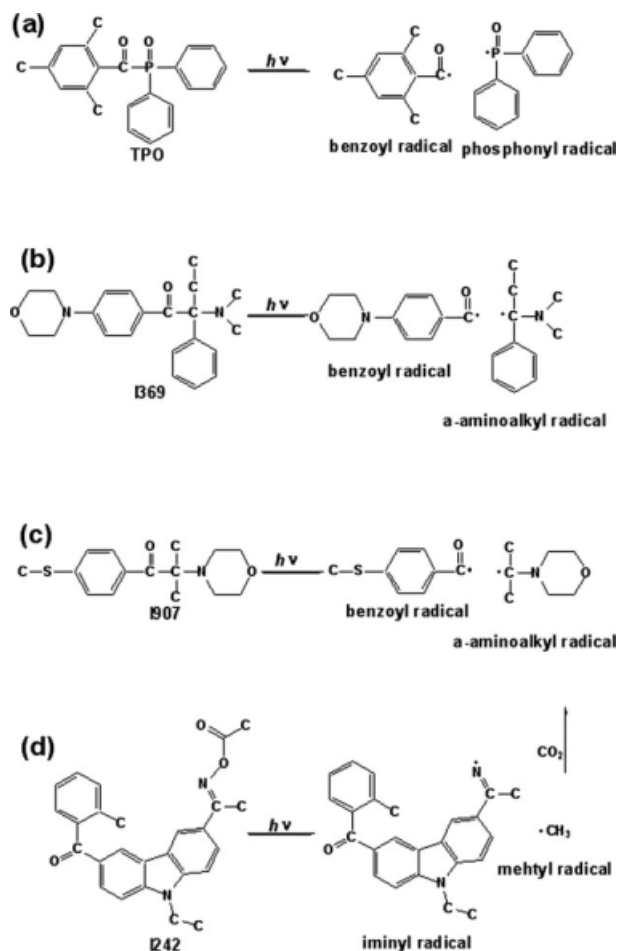
#### Influence of photoinitiator on the rate of polymerization of B2 with CB

Figure 10 shows that once CB was added into the B2/PI system, the  $R_p$  value decreases greatly, as compared to the results in Figure 8. This is because CB is a light-shielding material and also a radical scavenger as mentioned earlier. The decrease is at least one order in magnitude for those systems initiated by TPO, I907, and I369. However, the  $R_p$  of CB/B2 system initiated by I242 only decreases to one-third of the value of B2 system without adding CB. The  $R_{p,max}$  could still reach a value of  $1.05 \times 10^{-3}$  (s<sup>-1</sup>) for CB/B2 system by I242. As a result, the  $R_p$  value of the CB/B2 system initiated by TPO, originally the highest one in B2 system without adding CB, is even smaller than that by I242. To explain this behavior, the UV/visible absorption spectra of each PI (0.001% in PGMEA) and CB (0.001% in PGMEA), as well as the emission spectrum of light source were all recorded and compared (data not shown here). Subsequently, we define a ratio ( $F$ , %) as the amount of light absorbed by PI divided by the total amount of light absorbed by PI and CB as shown in the following equation.<sup>36</sup>

$$F = \left( \frac{\sum_{\lambda} I_{abs}^{\lambda}(PI)}{\sum_{\lambda} I_{abs}^{\lambda}(PI) + \sum_{\lambda} I_{abs}^{\lambda}(CB)} \right) \times 100\%$$

where  $I_{abs}^{\lambda}(x)$  is the light intensity absorbed by compound  $x$  (PI or CB) at wavelength  $\lambda$  and equals to  $N_{\lambda}(1 - 10^{-A_{\lambda}(x)})$ , where  $A_{\lambda}(x)$  is the absorbance of compound  $x$  at wavelength  $\lambda$ ,  $N_{\lambda} (= \frac{k \times I_{\lambda}^{em}}{hc\lambda \times N_A})$  is the amount of photons emitted from the UV lamp at

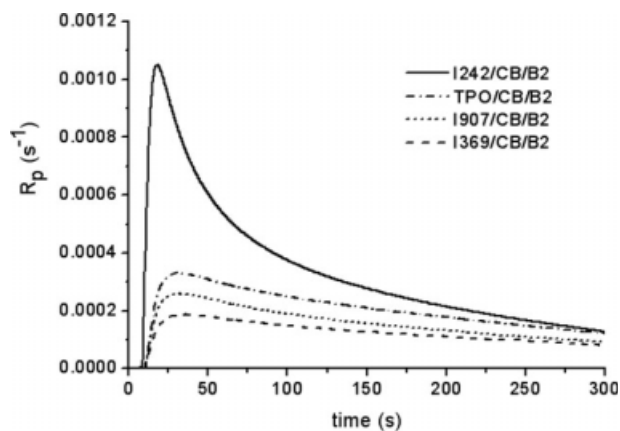




**Figure 9** Photocleavage mechanism of PIs: (a) TPO, (b) I369, (c) I907, and (d) I242.

wavelength  $\lambda$ ,  $k$  is a proportionality factor,  $I_{\lambda}^{\text{rel}}$  is the relative intensity of the UV lamp,  $h$  is Plank's constant,  $c$  is the light speed, and  $N_A$  is Avogadro's number. The  $F$  value is thus calculated from the absorbance spectra of PI and CB with the particle size of 104 nm in the wavelength range from 250 to 450 nm.

As seen in Table II, all  $F$  values are less than 20% indicating that most of the light is absorbed by CB. The highest  $F$  value, 16.7%, was found for the I242 initiator, thus explaining its fastest  $R_p$  in these four systems. For the same reason, the relatively small  $R_p$  found in the system with TPO is due to its relatively low value of  $F$ . Therefore, TPO is not suitable for the cure systems with CB although it is very efficient for photocure in the systems without CB. Besides,  $F$  values of I369 and I907 are 15.6 and 11.4%, respectively, which are higher than that of TPO. Unfortunately,  $R_p$  in the CB/B2 systems by these two PIs are relatively low, because they are not suitable for the resins with carboxylic acid group as explained previously. According to the results, I242 is thus a suitable PI



**Figure 10** The effect of different PIs on polymerization rate of B2 at 50°C in the presence of CB in a nitrogen atmosphere. The polymerization rate was measured by photo-DSC and the UV light intensity is 1.3 mW/cm<sup>2</sup>.

for the CB/B2 system and is therefore used for the following lithography study.

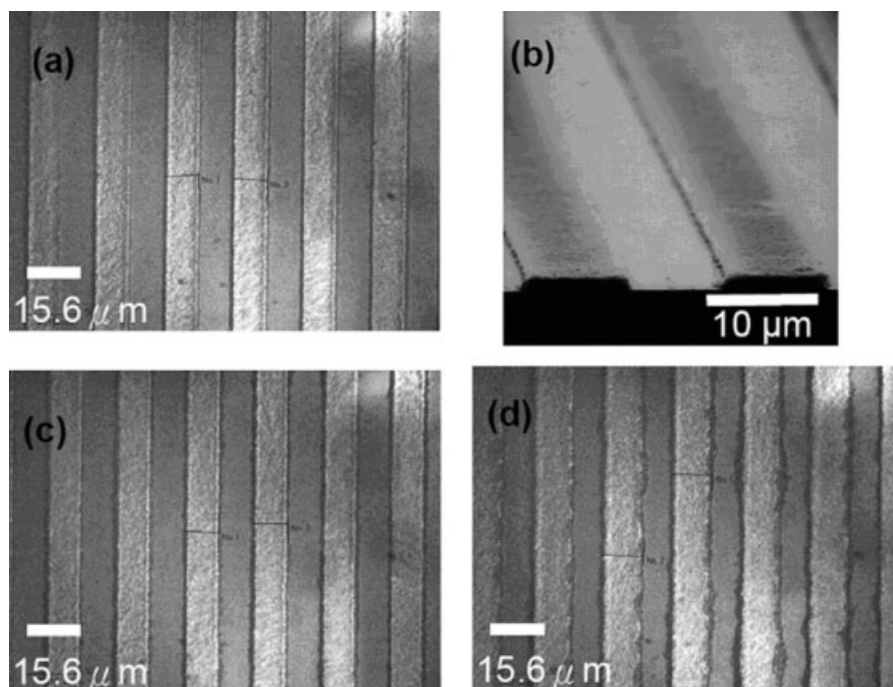
### UV-lithography property

The CB/B2 dispersion with the addition of I242 PI was used to prepare a black photoresist which could be useful for color filter in liquid crystal display. The black patterns with three different weight ratios of CB/B2, namely 4/6, 5/5, and 6/4 (wt/wt), upon UV irradiation of 200 mJ/cm<sup>2</sup> were prepared by using an UV-lithography process with a 10  $\mu$ m-stripe photo-mask. The exposure dose for the systems with CB was required to be at least 200 mJ/cm<sup>2</sup> in order to produce a good resolution of black pattern. Because of the acrylate and methacrylate double bonds in dispersant, the exposed area by UV-irradiation can be cured. Following that, the unexposed area can be easily washed out in an alkaline developer due to the carboxylic acid group in the dispersant (cf. Fig. 6). The advantage of this CB/B2 system is that no other curable resins are needed. Figure 11(a,b) displays the vertical view and cross-sectional image of black pattern developed from the system with a CB/B2 of 4/6 (wt/wt) by OM and SEM observation, respectively. A clean and straight black pattern of

**TABLE II**  
Fraction of Light ( $F$ ) Absorbed by Photoinitiator in the Presence of CB

Photoinitiator	$F$ (%)
I242	16.7
I369	15.6
I907	11.4
TPO	4.9

The  $F$  value is calculated from the absorbance spectra of PI and CB with the particle size of 104 nm in the wavelength range from 250 to 450 nm.



**Figure 11** The image of 10  $\mu\text{m}$  line-width and 1  $\mu\text{m}$  film-thickness of black pattern developed from the systems with different weight ratios of CB/B2 (a) 4/6 (wt/wt) by OM, (a) 4/6 (wt/wt) by SEM, (c) 5/5 (wt/wt) by OM, (d) 6/4 (wt/wt) by OM. Exposure dose = 200  $\text{mJ}/\text{cm}^2$ .

10  $\mu\text{m}$  in width and 1  $\mu\text{m}$  in thickness on the glass substrate is observed. In addition, a clear straight black pattern developed from the system with a CB/B2 of 5/5 (wt/wt) is also observed in Figure 11(c). By contrast, a black pattern from the system with a CB/B2 of 6/4 (wt/wt) shows larger line-width and poor resolution [Fig. 11(d)]. Therefore, as the content of B2 is lower such as in the system of CB/B2 = 6/4 (wt/wt), the unexposed area is not easily dissolved in the alkaline developer and thus the resolution of black pattern becomes poor.

### CONCLUSIONS

This research successfully prepared an effective dispersant for a high loading of CB with UV-curable and alkali-soluble properties. This dispersant, B2, can provide strong interaction with CB by its urethane, amide, and imide anchoring groups and enough steric hindrance by its long chain structure to prevent CB from aggregation. Therefore, a high loading of stable CB dispersion, 10 wt % CB in PGMEA, with a particle size of about 100 nm was obtained by using the B2 dispersant. With particle size of about 100 nm, the CB dispersion was thus suitable to be an effective light-shielding material for color filter in liquid crystal display and plasma display applications. In addition to providing the stability of CB in dispersion, (meth)acrylate and carboxylic acid functional groups in B2 impart its UV-curable and alkali-soluble properties. The CB/B2

dispersion with the addition of an efficient PI, I242, can therefore be used as a black photoresist. In general, a black pattern with a line-width of 20–30  $\mu\text{m}$  is sufficient for practical use. In this work, the successful preparation of black pattern with a high resolution of 10  $\mu\text{m}$  stripe pattern proves that B2 is an effective CB dispersant possessing both UV-curable and alkali-soluble properties, a promising material for applications in high-resolution color image.

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