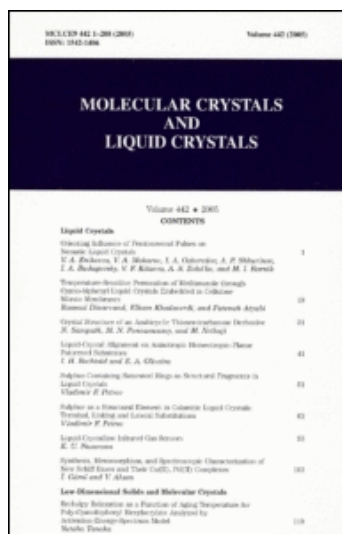


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Improving the Contrast Ratio of Red Pixels in Liquid-Crystal Displays by Synthesizing Synergists from an Anthraquinone Colorant

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The color properties of liquid-crystal displays are usually classified on the basis of color representations, contrast ratios, and brightness, which primarily depend on the properties of pigments. Among these classifications, the contrast ratio can be improved by minimizing the light scattering of the pigment particles, which is directly related to the degree of dispersion. Therefore, synergists are usually applied to increase the contrast ratio by augmenting the efficiency of the dispersion. In this study, synergists containing anthraquinone as a backbone were synthesized and then their performance in improving the contrast ratio was examined.

Keywords Anthraquinone; contrast ratio; liquid-crystal display; pigment; synergist

Introduction

Liquid-crystal displays (LCDs) are important devices in portable displays, monitors, and high-definition televisions, which require high resolution and good color properties to ensure good picture quality [1–4]. For such applications, LCDs have a color filter containing red, green, and blue pixels prepared from a polymeric binder and pigments [5]. During image processing in LCDs, the color filter determines the color properties, which are classified as the color purity (strength and representation), contrast ratio, and brightness.

Among these color properties, this study focused on the contrast ratio, which is important for ensuring a high picture quality. LCDs with a poor contrast ratio cannot show deep-black images; therefore, the contrast ratio of LCDs is considered to be an indicator of the grade of the LCDs in the market.

The contrast ratio is a numerical value that is obtained by dividing the maximum brightness by the minimum brightness. For a good contrast ratio, the light should

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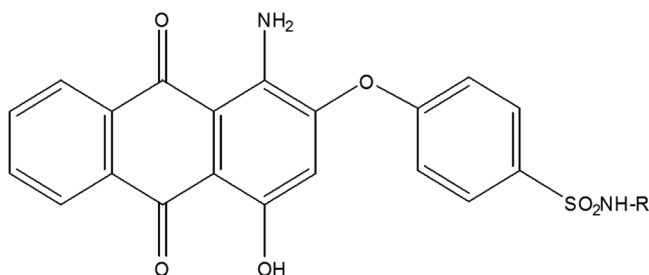


Figure 1. Structure of newly designed synergists derived from anthraquinone dye (CI Disperse Red 60).

not pass through when the polarizers are closed for a dark image. However, a small amount of light does pass through (known as *light leakage*), and this increases when the light is scattered by the particles of pigments. Therefore, to improve the contrast ratio, light scattering should be minimized by using particles with good physical properties such as uniformity of size, particle shapes, and small mean particle sizes [6,7]. These properties can be obtained via good dispersion of the pigment particles [8,9]. The dispersant used is important for ensuring a good dispersion process, but it has limitations with respect to ultrafine particles for color filters. Accordingly, a powerful synergist is necessary to aid dispersion of ultrafine particles. As a result, many pigment paste manufacturers are developing synergists that are more efficient [10].

The use of synergists as additives usually improves the efficiency of dispersion by preventing the agglomeration of particles. This facilitates the occurrence of an intense process that improves the physical properties of the particles. In the present study, the four synergists shown in Fig. 1 were prepared from the anthraquinone and made to react with chlorosulfonic acid and corresponding alkyl amines. The purity and chemical structures of each synergist were then assessed by nuclear magnetic resonance (NMR) and mass spectra.

In this article, we discuss the performance of the synergists in improving the contrast ratio. In addition, the effects of the synergists developed herein were compared with those of a commercial synergist. For this study, pigment pastes were prepared from these synergists and the particle sizes, distributions, and viscosities of the pastes were analyzed for their dispersion performances. Finally, color filter photoresists (CFPRs) were prepared from the pigment pastes and corresponding additives were used to measure and evaluate the contrast ratio.

Experimental

Equipment

The molecular masses of the synergists were measured using a JMS600 W mass spectrometer (JEOL, Tokyo, Japan). The chemical structures and purity of the synergists were analyzed using a 500 MHz NMR (Avance II 500, Bruker BioSpin GmbH, Rheinstetten, Germany). The λ_{max} of the synergist was measured using an ultraviolet (UV)-visible spectrophotometer (UV-1601, Shimadzu Corp., Kyoto, Japan).

The color properties and transmittance spectra were measured using an MCPD 3700 photodetector (Otsuka Electronics Co. Ltd., Osaka, Japan). The values of the contrast ratios were recorded using a contrast tester (CT-1, Tsubosaka Electric Co.

Ltd., Tokyo, Japan). A spin-coater (Sungwon Electronics Co. Ltd., Daejeon, Korea) was used to coat the CFPRs onto glass substrates. The particle sizes of the pigments were recorded using a particle size analyzer (Par III, Otsuka Electronics Co. Ltd., Osaka, Japan). The thicknesses of the coated materials on glass were measured using a profiler (Alpha-step IQ, KLA-Tencor Corp., Milpitas, CA, USA). A photomask aligner (MDE-400, Midas System Co. Ltd., Daejeon, Korea) was used for UV-curing of the CFPRs.

Materials

CI Disperse Red 60, which is an anthraquinone that was a pure chemical without dispersant, was supplied by Eastwell Co. Ltd. (Seoul, Korea). Chlorosulfonic acid, 2-ethylhexylamine, hexylamine, cyclohexylamine, and 3-diethylaminopropylamine were supplied by Sigma-Aldrich Inc. (St. Louis, MO, USA). CI Pigment Red 254 (Irgaphor Red BT-CF, Ciba Specialty Chemicals Inc., Basel, Switzerland) was employed in this study. The glass (370 mm \times 470 mm \times 0.63 T, 5 K Super) used as a coating substrate in this study was manufactured by Samsung Corning Precision Materials Co. Ltd., (Seoul, Korea). The glass was cut into suitable fragments (5 cm \times 5 cm) for the coating tests. The dispersant, Disperbyk 163, which was used to grind the pigments, was manufactured by BYK-Chemie GmbH (Kempen, Germany). The commercial synergist used for the comparison was Solspers 22000 (Lubrizol Corp., Wickliffe, OH, USA). Chemicals for preparation of a color filter photoresist included dipentaerythritol penta/hexaacrylate as a multifunctional monomer (Sigma-Aldrich Inc., St. Louis, MO, USA), Irgacure-369 as a photoinitiator (Ciba Specialty Chemicals, Inc., Basel, Switzerland), and FC-4432 as a surfactant (3M Company, St. Paul, MN, USA). A binder for preparation of the color filter photoresist was synthesized using benzyl methacrylate and methacrylic acid (Sigma-Aldrich Inc., St. Louis, MO, USA).

Synthesis of the Chlorosulfonated Anthraquinone. Sixty grams of anthraquinone was added carefully to 240 mL of chlorosulfonic acid and then cooled. When the addition was finished, the temperature was increased to 80°C and the mixture was stirred for 4 h at that temperature. The reaction was then checked by thin-layer chromatography (TLC; n-hexane/ethyl acetate, 3:1), after which 300 g of isopropyl alcohol was added carefully to quench the excess chlorosulfonic acid in an ice-water bath to prevent overheating. Finally, the mixture was poured into 1 L of ice water, and the precipitation was then filtered using Whatman filter paper No. 5. The collected reddish brown solid was washed with plenty of water and dried in air. The yield was 87%.

Synthesis of Synergists.

4-[1-Amino-9,10-dihydro-4-hydroxy-9,10-dioxo-2-anthracenyl]oxy]-n-(2-ethylhexyl)-benzenesulfonamide (**S1**). The chlorosulfonated product (8.6 g, 0.02 mol) was dissolved in 45 g of dimethylformamide (DMF) solvent, and a mixture of 2-ethylhexylamine (2.56 g, 0.02 mol) and triethylamine (2.0 g, 0.02 mol) was then added for 1 h. The temperature was then raised to 50°C and the resulting solution was stirred for 2 h. The reaction was then evaluated by TLC (n-hexane/ethyl acetate, 3:1), after which 45 g of methanol and 15 g of water were added to induce precipitation. The precipitated reddish brown solid was filtered using Whatman filter paper No. 5 and then dried in air. The yield was 82%. The chemical structure was identified by mass spectroscopy, which revealed peaks at 313, 330, 423, and 522 (100%, M⁺). Additionally, the NMR

spectra for identification of structure and purity showed peaks in CDCl_3 of δ 0.9–1.0 (m, 6H, $-\text{CH}_3$), 1.1–1.2 (m, 6H, $-(\text{CH}_2)_3-$), 1.3–1.4 (m, 2H, $-\text{CH}-\text{CH}_2-$), 1.4–1.5 (m, 1H, $-\text{SO}_2\text{NHCH}_2\text{CH}_2-$), 2.9–3.0 (q, 2H, $-\text{SO}_2\text{NH}-\text{CH}_2-$), 4.5 (t, 1H, $-\text{SO}_2\text{NH}-$), 6.5 (s, 1H, anthraquinone), 7.3 (d, 2H, phenoxy), 7.7 (m, 2H, anthraquinone), 7.9 (d, 2H, phenoxy), 8.3 (t, 2H, anthraquinone), and 13.8 (s, 1H, anthraquinone OH).

4-[(1-Amino-9,10-dihydro-4-hydroxy-9,10-dioxo-2-anthracenyl)oxy]-N-(hexyl)-benzenesulfonamide (**S2**). Preparations were prepared using the same method for **S1** with 2.0 g (0.02 mol) of hexylamine instead of 2-ethylhexylamine. The yield was 83%. The chemical structure was identified by mass spectroscopy, which revealed peaks at 313, 330, 346, and 494 (100%, M^+), and ^1H NMR (CDCl_3 , 500 MHz), which revealed peaks at δ 0.9–1.0 (t, 3H, $-\text{CH}_3$), 1.2–1.4 (m, 6H, $-(\text{CH}_2)_3-$), 1.4–1.5 (m, 2H, $-\text{SO}_2\text{NHCH}_2\text{CH}_2-$), 3.0–3.1 (q, 2H, $-\text{SO}_2\text{NHCH}_2-$), 4.7 (t, 1H, $-\text{SO}_2\text{NH}-$), 6.5 (s, 1H, anthraquinone), 7.3 (d, 2H, phenoxy), 7.7 (m, 2H, anthraquinone), 7.9 (d, 2H, phenoxy), 8.3 (t, 2H, anthraquinone), and 13.8 (s, 1H, anthraquinone OH).

4-[(1-Amino-9,10-dihydro-4-hydroxy-9,10-dioxo-2-anthracenyl)oxy]-N-(3-diethylaminopropyl)-benzenesulfonamide (**S3**). Preparations were made using the same method for **S1**, with 2.6 g (0.02 mol) of 3-diethylaminopropylamine instead of 2-ethylhexylamine. The yield was 75%. The chemical structure was identified by mass spectroscopy, with peaks at 86 (100%), 129, 330, and 523 (M^+) being observed, and by ^1H NMR (CDCl_3 , 500 MHz), which revealed peaks at δ 1.0–1.1 (t, 6H, $-\text{N}(\text{CH}_2\text{CH}_3)_2$), 1.6–1.7 (q, 2H, $-\text{SO}_2\text{NHCH}_2\text{CH}_2-$), 2.5–2.6 (m, 6H, $-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2)_2-$), 3.1–3.2 (t, 2H, $-\text{SO}_2\text{NHCH}_2-$), 6.5 (s, 1H, anthraquinone), 7.3 (d, 2H, phenoxy), 7.7 (m, 2H, anthraquinone), 7.9 (d, 2H, phenoxy), 8.3 (t, 2H, anthraquinone), and 13.8 (s, 1H, anthraquinone OH).

4-[(1-Amino-9,10-dihydro-4-hydroxy-9,10-dioxo-2-anthracenyl)oxy]-N-(cyclohexyl)-benzenesulfonamide (**S4**). Preparations were conducted using the same method used for **S1**, with 2.0 g (0.02 mol) of cyclohexylamine instead of 2-ethylhexylamine. The yield was 82.5%. The chemical structure was identified by mass spectrometry, which revealed peaks at 313, 330, 346, and 492 (100%, M^+), as well as by ^1H NMR (CDCl_3 , 500 MHz), which showed peaks at δ 1.1–1.3 (m, 5H, axial H cyclohexane), 1.6 (d, 1H, equatorial H cyclohexane), 1.7 (d, 2H, equatorial H cyclohexane), 1.8 (d, 2H, equatorial H cyclohexane), 3.2–3.3 (m, 1H, $-\text{SO}_2\text{NHCH}-$), 4.6–4.7 (d, 1H, $-\text{SO}_2\text{NH}$), 6.5 (s, 1H, anthraquinone), 7.3 (d, 2H, phenoxy), 7.7 (m, 2H, anthraquinone), 7.9 (d, 2H, phenoxy), 8.3 (t, 2H, anthraquinone), and 13.8 (s, 1H, anthraquinone OH).

Preparations of Pigment Pastes. Fifteen grams of CI Pigment Red 254 were stirred with 15 g of a dispersant (Disperbyk 163, active ingredient 45%), 0.5 g of each synergist, and 69.5 g of propylene glycol monomethyl ether acetate (PGMEA; Aldrich Chemicals) for about 1 h during the wetting process.

CI Pigment Red 254 and the synergists were employed when preparing the pigment pastes. The mixture was ground using a stirrer (220 v/120 w, 0–4,700 rpm, custom-made) with 300 g of zirconia beads (0.3 mm), a gear-shaped agitator with 7 cm diameter, an ice-water bath, and a plastic jar with 9 cm diameter and 10 cm height. The rotation speed was about 3,000 rpm and the pigment paste was cooled to 15–20°C during grinding. The beads were filtered using a sieve to collect the pigment paste. Particle size was analyzed using a particle size analyzer.

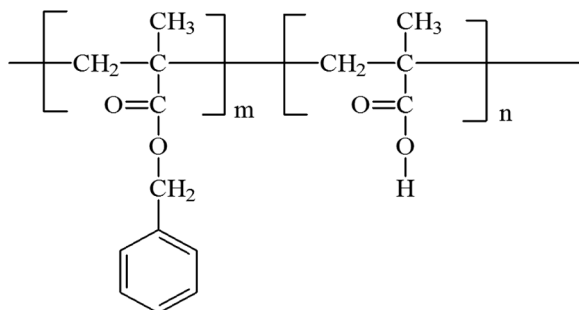


Figure 2. Structure of the polymeric binder containing carboxylic acid group for alkali development.

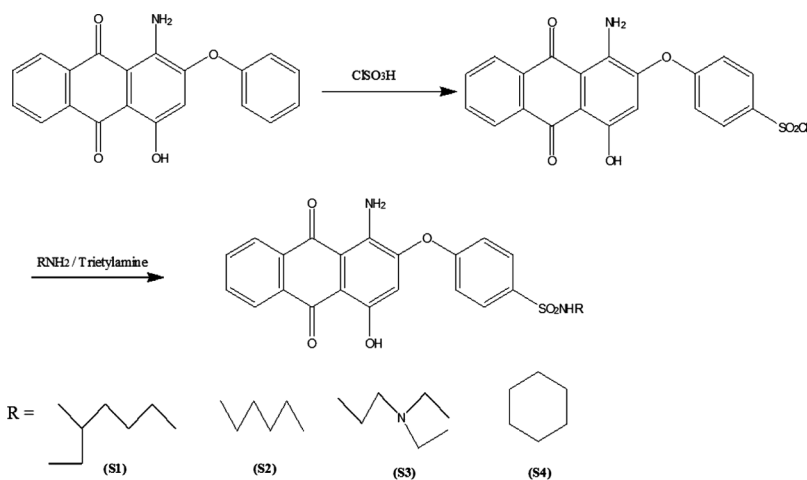
Synthesis of Poly(Benzyl Methacrylate-co-methacrylic Acid). Methacrylic acid (6.9 g, 0.08 mol) and benzyl methacrylate (33.1 g, 0.19 mol) were stirred into 60.0 g of PGMEA under nitrogen purging to expel the oxygen. The polymerization was conducted at 90°C for 5 h using 2.0 g of 2,2'-azobisisobutyronitrile (Junsei Chemicals, Japan) as a radical initiator. The viscosity of the polymer mixture was 368 cP at 25°C, and the content of the polymer was about 37%. The mixture was used as a binder solution without isolation of the polymer. The polymer structure shown in Fig. 2 had values of m and n representing 7 and 3, respectively.

Preparation of Color Filter Photoresists (CFPR). The pigment paste (40.0 g), binder solution (13.5 g), dipentaerythritol penta/hexaacrylate (5.0 g), Irgacure-369 (1.0 g), and FC-4432 (0.1 g) were mixed with 40.4 g of PGMEA. This mixture was stirred for 1 h in a dark room and then filtered with a membrane polytetra fluoroethylene (PTFE) filter (porosity 1.0 μm).

Preparation of Test Glass Sheets. A small glass sheet (5 cm \times 5 cm) was coated with the CFPRs using a spin coater at an adequate rpm for 10 s to control the thickness of the thin layer. The coated glass was prebaked to evaporate the solvent at 80°C for 90 s. UV exposure was applied without a photomask at 200 mJ/cm² at 360 nm. The development process for generating pixels was skipped, and the post-bake process consisted of 30 min at 220°C. Each test glass sheet was measured to evaluate the CIE Yxy value of the color coordination using the MCPD-3700 instrument and to evaluate the contrast ratio using the CT-1 equipment.

Results and Discussion

Anthraquinone was selected as a backbone for several reasons. First, it has a suitable chemical structure that contains carbonyl, amine, and hydroxyl, which enables hydrogen bonding with the pigments. In addition, it contains phenoxy to induce sulfonyl groups, which are essential for polarity and connection with nonpolar bulky hydrocarbons [7]. Second, anthraquinone has a similar color to CI Pigment Red 254, which is a common colorant of red pixels in LCDs. Even though a small quantity of synergist is applied, it can influence color properties that are sensitive to the CIE xy color coordination. For this reason, synergists with a blue color are not suitable for red pigment dispersion.



Scheme 1. Synthetic route for synergists S1, S2, S3, and S4.

Third, CI Disperse Red 60 is an anthraquinone that is readily available in the market and reasonably priced. In addition, nonpolar hydrocarbons containing six or eight carbons were selected for an easier manufacturing process. In contrast, hydrocarbons with a higher number of carbons, such as oleylamine, are not suitable for obtaining a pure product because an oily product makes solidification and precipitation difficult when precipitated by water and methanol in DMF.

The synergists used in this study were synthesized as shown in Scheme 1, and the chemical structures and purities of the target products were identified by mass spectra and 500 MHz NMR spectra.

To synthesize the synergists, chlorosulfonic acid was employed to introduce the chlorosulfonyl group at the para position of the phenoxy substituent. This reaction was relatively easy but should be conducted carefully. Quenching of excess chlorosulfonic acid with isopropyl alcohol should be conducted in an efficient cooling system, unless purity and yield deteriorate due to excessive heat. The reaction and purity were checked by TLC (n-hexane/ethyl acetate, 3:1), and the yield was quite good (87%).

2-Ethylhexyl amine, hexylamine, 3-diethylaminopropylamine and cyclohexylamine were used for the introduction of the nonpolar alkylamines. An $\text{S}_{\text{N}}2$ type reaction for alkylation was conducted in an aprotic polar solvent such as DMF, giving products with an acceptable yield of 80–70%. In terms of solubility and reactivity, DMF is a suitable reaction medium. Precipitation by methanol and water was also a good combination for obtaining pure synergists. Mass spectroscopy was used to identify chemical structures and provide exact molecular peaks (Fig. 3).

The chemical structure and purity of the synergists were also assessed by NMR spectra as shown in Fig. 3, which shows good purity and exact chemical structures. Specifically, the hydrogen of the hydroxy on anthraquinone appears as a singlet peak in a much lower field near 14 ppm, which indicates the formation of a six-membered ring with the neighboring carbonyl through a tight hydrogen bond. The hydrogen on C3 of anthraquinone appears as a singlet peak at 6.5 ppm, the four hydrogens on C6–9 of anthraquinone appear as two multiplet peaks at 7.8 and 8.3 ppm, and the

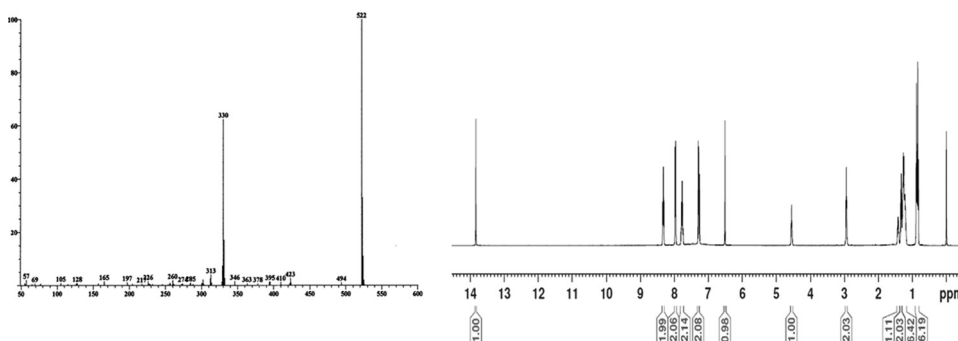


Figure 3. NMR and mass spectra of the synergist S1.

four hydrogens on phenoxy appear as two doublet peaks at 7.3 and 7.9 ppm. As expected, many hydrogens in alkyl groups appear as complex peaks in the upfield region around 1–3 ppm, with the exact integration value of hydrogens. In addition, the NMR spectrum of the starting material showed a proton on the *para* position as a doublet of doublets around 7.3 ppm, and the proton peak disappeared after the sulfonamide formation. Therefore, we can show that the sulfonamide is introduced exactly into the *para* position of the phenoxy group.

The dispersion of CI Pigment Red 254 with a small quantity of each synergist was processed into the PGMEA with the BYK 163 dispersant, which was a known urethane type. Each of the dispersions was conducted for 5 h with a strong shear rate using zirconia beads under the same conditions for the purposes of comparison.

CI Pigment Red 254 was supplied by Ciba Specialty, which is the only supplier for LCD use; thus, the red pigment is the standard product in the industry. A small quantity of synergists (about 0.5% per total weight of mixture) was used in this study. A synergist is an additive for improving dispersion, and a small quantity is recommended to prevent side effects of color changes, because most synergists are derivatives of dyes and pigments with their own colors.

The physical properties of pigment particles for a good contrast ratio can be achieved by dispersion with an effective shear rate, but this gives rise to easy agglomeration due to smaller particle sizes causing a large surface area. Thus, the role of the synergist is essential for increasing the efficiency of the dispersion and stability by anchoring the dispersants to the pigments as shown in Fig. 4. Accordingly, many pigment paste manufacturers have recognized the importance of synergists for obtaining a high-contrast ratio for LCDs. Consequently, synergists are agents for surface treatment that adhere to the surface of a pigment and then augment the efficiency of dispersion by anchoring the dispersants tightly with an affinity that includes hydrogen bonds [7]. The resulting performance of the synergists for dispersions was measured based on the average particle size and distribution and the viscosity of the paste solutions (Table 1).

As shown in Table 1, the prepared synergists gave excellent performance in terms of average particle sizes when compared with the commercial synergist Solsperse 22000 supplied by Lubrizol Ltd., which is a polymer colorant with a red-dish yellow color. The commercial synergist is widely used to prepare pigment pastes for traditional and LCD uses, which is one of reasons for its selection [11]. The synergist S3 containing 3-diethylaminopropylamine showed the smallest particle size

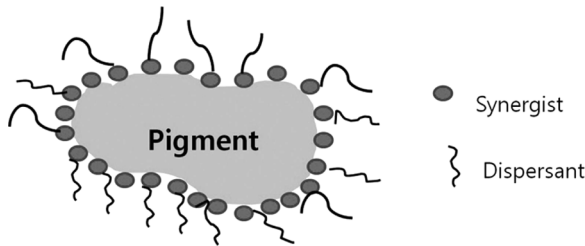


Figure 4. Role of synergist adhering to surface of pigment for anchoring dispersant.

of 54.7 nm, but the gap was not great when compared with synergists **S1** and **S2**, which had sizes around 59.0 nm. However, the difference in dispersion efficiency between the commercial and the prepared synergists was quite large, with the commercial synergist having an average particle size of 78.2 nm. In terms of size distributions, **S1** had the smallest D10 at 18.8 nm and the other synergists, **S2** and **S3**, as well as the commercial synergist had a D1 of around 27–47 nm of D10. However, the D90 of the commercial synergist was 828.7 nm, which was much bigger compared to those of the prepared synergist, which was around 100–240 nm. These results for sizes and distributions explained the excellence of the prepared synergists in this dispersion system for LCDs.

The viscosity of the paste can provide more evidence of the dispersion performance. The paste prepared from the synergist had a low viscosity in the range of 5.32–6.01 cP, whereas the commercial synergist had much higher viscosity at 9.8 cP. In general, pigment paste with good dispersion showed a lower viscosity due to the decrease in interactions between particles.

To evaluate the contrast ratio of each synergist, CFPRs were prepared from the pastes, which are a negative photoresist. The amounts of other ingredients in the final composition were as follows: 6.0% pigment, 2.7% dispersant, 5% multifunctional monomer, 5% binder polymer, 0.1% fluorosurfactant, and 1.0% UV curing agent, with the remainder being PGMEA solvent. The final composition of solid materials in the photoresist was around 20% by weight. CIE Yxy color coordination for each glass sheet was measured using an MCPD-3700 spectrophotometer (Table 2).

As shown in Table 2, all CFPRs manufactured from the synergists, including the commercial synergists, met the exact target value of CIE xy color coordination, with

Table 1. Properties of the Pigment Pastes Prepared using the Synergists

Synergist	Average particle size (nm)	Particle size distribution (nm)			Viscosity (cP) at 22°C
		D10	D50	D90	
S1	59	18.8	70.4	235.9	5.86
S2	58.2	27.5	67.6	112	5.32
S3	54.7	29.1	55.3	109.2	5.38
S4	59.7	46.2	65.7	88.8	6.01
Solsperse 22000	78.2	47.2	66	828.7	9.8

Table 2. Color Coordination of CIE Yxy Value of CFPR Prepared from the Synergists

CFPR	Y	x	y
CR-S1	19.727	0.653	0.335
CR-S2	19.964	0.652	0.337
CR-S3	20.305	0.653	0.337
CR-S4	20.066	0.654	0.335
CR-Solsperser	20.737	0.650	0.333

an x around 0.65 and y around 0.33. These values were essential for HDTV with 72% color representation. However, in terms of brightness, the Y values of the synergists were slightly poorer than those of the commercial synergist, but this difference was small. More precisely, the synergist **S1** showed the poorest value, 19.727, whereas **S3** showed a better value of 20.305 and the commercial synergist had the best value, 20.737. These results came from the color of the synergist itself. The color of Solsperser 22000 was bright yellow, with λ_{\max} at 415 nm, but the synergists were bluish red with λ_{\max} at around 518–514 nm (Table 3), which decreased the brightness of the Y value. Among the synergists, **S3** had a withdrawing effect on nitrogen in the alkyl groups, resulting in a slight hypsochromic effect with λ_{\max} at 514 nm, which created a slightly better Y value.

Finally, to evaluate the contrast ratio, the glass sheets prepared from the synergists were measured using a contrast tester (CT-1) and the values are listed in Table 4. The reference value was 10,000, which is based on bare glass. The data for the contrast ratios were collected and are listed in Table 4. All prepared synergists showed contrast ratio values of more than 2,200, especially synergists **S1**, **S2**, and **S3**, which contained bulky alkyl chains that gave rise to values around 2,500. These values were twice as high as that of the commercial synergist (1,337).

For a good contrast ratio, the minimum brightness was more crucial than the maximum brightness. Specifically, all prepared synergists had a minimum brightness of less than 0.1, and the commercial synergists had the poorest brightness of about 0.223, even though the commercial synergists had a better maximum brightness of 298.2.

A key for a better contrast ratio is to minimize the minimum brightness by decreasing the light leakage rather than to maximize the maximum brightness. Based on the characteristics of LCDs, it is difficult to increase the maximum brightness because this requires improvement of the light source device or dilution of the color concentration, which is prevented due to limitations of power consumption and poor color representation. Figure 5 is helpful in understanding the relationship between the chemical structure and the contrast ratio.

Bulky and nonpolar alkyls performed better in terms of the contrast ratio (Fig. 5). The synergists containing bulky alkyl chains such as 2-ethylhexyl, hexyl,

Table 3. λ_{\max} of Synergists in Acetone

Synergist	S1	S2	S3	S4	Solsperser 22000
λ_{\max} (nm in acetone)	518	516	514	516	415

Table 4. Contrast Ratio Values of CFPRs Prepared from the Synergists

CFPR	Contrast ratio (max/min value)	Maximum Value	Minimum value
CR-S1	2,585	227.46	0.088
CR-S2	2,544	231.5	0.091
CR-S3	2,487	226.3	0.091
CR-S4	2,289	226.58	0.099
CR-Solsperse	1,337	298.2	0.223

and 3-diethylaminopropyl yielded a better contrast ratio of around 2,500 when compared with that of synergists containing compact alkyl groups such as cyclohexane (2,289). These results clearly showed that synergists with bulkier alkyls produced a better contrast ratio and may explain why bulky alkyls have more effective steric repulsion, resulting in the better stability of pigment particles.

There are two methods of stabilizing particles: one is electrostatic repulsion in an aqueous system and the other is steric repulsion in an organic solvent system [2]. Undoubtedly, the most important role of synergists is to anchor dispersants to pigments. Additionally, it has been found that a bulky structure could play an important role in stabilization via steric repulsion in a fashion similar to that of usual dispersants. More precisely, compact alkyls such as cyclohexyl had the poorest contrast ratio of 2,289 when compared with bulky alkyl groups, such as that of 2-ethylhexyl, which was 2,585. Interestingly, S1 had a slightly larger average particle size (59 nm) than that of S3; however, it had a better contrast ratio than S3. These results demonstrate that evaluation of contrast ratio not only depends on particle size but also on other properties such as distribution and the shapes of the particles. It can be concluded that the inclusion of a suitable chemical structure such as anthraquinone as the backbone for anchoring is most important. Moreover, the inclusion of a bulky structure for steric repulsion is important in terms of fine-tuning a high contrast ratio.

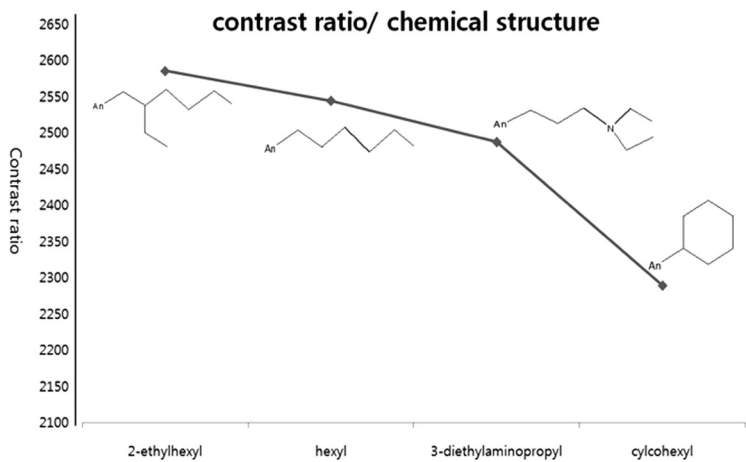


Figure 5. Relationship between contrast ratio and synergist chemical structure.

Conclusion

We found that synergists prepared from anthraquinone colorant as the backbone were excellent for improving contrast ratios, producing values greater than 2,500, whereas that of the commercial synergist was 1,300. As the authors expected, the synergists had a better contrast ratio due to the anchoring effect of anthraquinone and the bulkiness of the nonpolar portion of the synergists. Therefore, alkyl groups containing more than 9–10 carbons will be prepared and tested for comparison with the current results obtained from 6–8 carbon alkyls. The synergists evaluated in the present study were inferior in terms of brightness due to their bluish red color; thus, the introduction of noncolored or brighter anthraquinone moieties will be worthwhile.

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