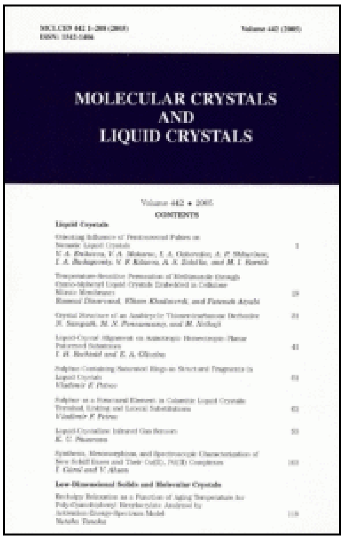

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Effect of the Addition of Acrylic Monomers on Mechanical Properties of Patterns Applied in Negative-Type Photoresists

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Typically, a negative-type photoresist consists of a polymer binder, polyfunctional monomer (or cross-linker), photo initiator, solvent, and additives. A series of acrylic monomers was prepared as cross-linkers using dipentaerythritol hexa-acrylate (DPHA) and blending monomers with n-butyl methacrylate (BuMA), benzyl methacrylate (BzMA), and acrylic-silica sol (Pro-1264), and the mechanical properties of patterns were studied. The elastic recovery and the compression of the patterns were measured using a dynamic ultra-micro-hardness tester. Patterns of the photo spacer were observed using a scanning electron microscope. Superior mechanical properties (elastic recovery, compression, and surface hardness) of the patterns and the optimum recipe could be obtained by adding 2 wt% of acrylic monomers (BuMA or BzMA or Pro-1264) to the photoresists when DPHA was fixed at 10 wt%. An inverted conical pattern was observed when 3 wt% of Pro-1264 was added to the photoresists when the transmittance of patterns worsened because of the low capacity of the interpenetration network.

Keywords Acrylic monomer; compression; elastic recovery; negative-type photoresist

Introduction

A dramatic growth of thin-film transistor liquid crystal displays (TFT–LCD) has been supported by a strong demand for flat-panel displays in applications such as TVs, monitors, and notebooks. In accordance with the demands for new generation TFT–LCD technology, improvements in the performance of a color filter and a liquid-crystal layer are concerned with the contrast, brightness, color saturation, uniformity, response time, and hardness [1,2]. In the conventional process, spacer beads (plastic or inorganic fine particles) agglomerate and distort the contrast ratio and the light leakage. Therefore, a photo spacer (a column fixed by photo lithography) plays an important role in controlling the thickness and uniformity control between the color filter and the TFT array substrate.

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Typically, a negative-type photoresist consists of a polymer binder, polyfunctional monomer (or cross linker), photo initiator, solvent, and additives [2–4]. The mechanism of the negative-type photoresist is that when it is exposed to photoirradiation, the exposed area cannot subsequently be removed in an alkaline developer. After development, the desired pattern is formed on a substrate. The structure and characteristics of polymer binders and cross-linkers, intensity of the interpenetration network, and the proportions of the polymer binder influence the mechanical properties of the photo spacer. The main function of the photo spacer is to separate the TFT array and color filter substrate to lead liquid-crystal drops to fill defined gaps (approximately 3–5 μm). Therefore, the photo spacer is necessary for excellent mechanical properties; i.e., elastic recovery > 70%, compression > 200 mN, and surface hardness > 3H. Avoid the damage being caused by external force. Properties of acrylic copolymers, such as their photosensitivity [5], thermal stability [6–9], pattern resolution [9,10], glass transition temperature [11], nanosilica modified [8,12–14], and physical characteristics [15] have been investigated in the negative-type photoresists. However, regarding the elastic recovery and compression behavior of photo spacers, studyies have not yet been sufficient. In order to study the effect of the content of a polyfunctional monomer or blending one monomer with another acrylic monomer on the mechanical behavior of patterns applied in negative-type photoresists, a series of acrylic monomer was prepared as cross-linkers and the mechanical properties of the resulting patterns were studied.

Experiment

Materials

Materials used in this experiment include dipentaerythritol hexa-acrylate (DPHA), n-butyl methacrylate (BuMA), benzyl methacrylate (BzMA), and potassium hydroxide (KOH). All were reagent grade and purchased from Aldrich. Pro-1264 acrylic-silica monomer (Procachem), polymer binder (poly(methacrylic acid-co-styrene-co-glycidal methacrylate), Mw = 13,000, PDI = 2.5, EVERLIGHT Chemical Co.), propylene glycol monomethyl ether acetate (PGMEA, Dow Chemical), 2-benzyl-2-dimethyl-amino-1-(4-morpholinophenyl)butanone (I-369, Ciba-Geigy), isopropyl thioxanthone (ITX, Ciba-Geigy), R-08 (Dainippon Ink and Chemicals), polyfunctional monomer (TO-2355, TOAGOSEI), all of which were certified grade.

Photoresists Preparation

Negative-type photoresists were prepared by mixing of a polymer binder (15 wt%), polyfunctional monomer (DPHA, ca. 10 wt%), blending monomer (BuMA or BzMA or Pro-1264, 1–3 wt%), photo initiator (I-369, 6 wt% and ITX, 2 wt%), solvent (PGMEA, 65 wt%), and surfactant (R-08, 0.05 wt%) at room temperature for 6 h, and then the photoresists were filtered through a 2-μm filter (Table 1).

Lithographic Process

1. Photoresist coating on super twisted nematic (STN) glass (75 × 75 mm) using a spin coater (500 rpm for 10 s).
2. Prebaking at 90°C for 10 min in an oven.

Table 1. Compositions and mechanical properties

Sample name	DPHA (wt%)	BuMA (wt%)	BzMA (wt%)	Pro1264 (wt%)	Elastic recovery (%)	Compression (mN)	Surface hardness	Thickness (μm)
DPHA-70	7.0	0	0	0	80.7	225	3H	4.4
DPHA-85	8.5				80.5	200	3H	4.7
DPHA-100	10.0				72.0	200	3H	4.9
DPHA-115	11.5				74.2	200	3H	4.5
DPHA-130	13.0				75.0	175	3H	4.4
BuMA-0	10.0	0	0	0	72.0	200	3H	4.9
BuMA-10		1.0			79.2	200	3H	4.8
BuMA-20		2.0			75.6	175	3H	4.7
BuMA-30		3.0			69.9	175	3H	4.7
BzMA-0	10.0	0	0	0	72.0	200	3H	4.9
BzMA-10			1.0		80.5	200	3H	5.0
BzMA-20			2.0		81.0	200	4H	5.2
BzMA-30			3.0		69.6	200	4H	5.0
Pro1264-0	10.0	0	0	0	72.0	200	3H	4.9
Pro1264-10				1.0	75.5	175	3H	5.0
Pro1264-20				2.0	76.2	175	4H	4.9
Pro1264-30				3.0	78.6	175	4H	5.2

3. Ultraviolet (UV) exposure (150 mJ/cm^2) with a contact mask (100-μm gap).
4. Development in 0.05 wt% potassium hydroxide (KOH) aqueous solutions at 25°C for 2 min.
5. Hard-baking at 230°C for 30 min in an oven.

Measurements

1. Elastic recovery. The cylindrical pattern (diameter = 20–25 μm, height = 4–5 μm) was measured using a dynamic ultra-micro-hardness microcompression tester (DUMH indenter, Shimadzu DUH-W201S, Fig. 1) with a force of 10 mN. The loading speed was 0.36 mN/s, and the holding time was 5 s. The elastic recovery (%) was calculated according to the following expression: Elastic recovery (%) = (D1/D2) × 100% (Fig. 2).
2. Compression. The cylindrical pattern (diameter = 20–25 μm, height = 4–5 μm) was measured by using a dynamic ultra-micro-hardness (DUMH) indenter, the

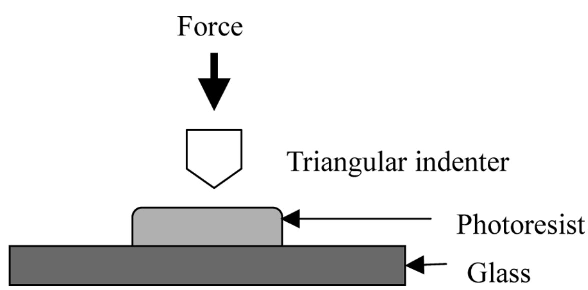

Figure 1. The DUMH indenter.

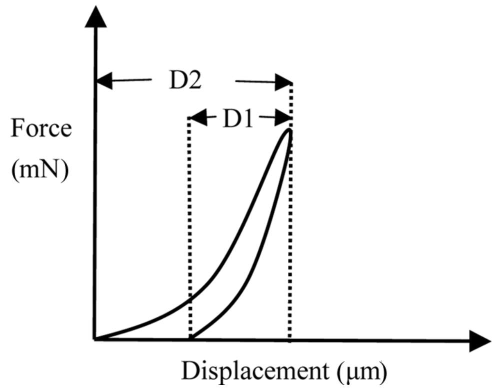

Figure 2. The elastic recovery graph.

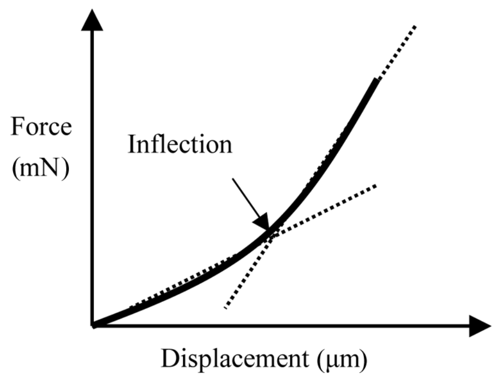

Figure 3. The compression graph.

loading speed was 17.65 mN/s, and the holding time was 5 s. The compression of pattern was calculated according to the inflection point of the curve (Fig. 3).

3. Surface hardness. The surface hardness of the films was examined by using an industrial pencil hardness test (Mitsubishi Uni Pencil).
4. Pattern thickness. The thickness of the patterns was measured by using a surface profiler (Taylor Hobson Form Talysurf series 2).
5. Pattern image. The image of the patterns was observed by using a scanning electron microscope (SEM, Hitachi S-4200).
6. Transmittance. A multichannel photo detector (MCPD, Photon MCPD-3000) measured the transmittance of patterns.

Results and Discussion

The latest technology of photo spacers was adopted in the negative-type photoresist, which was fabricated into the defined patterns by using a lithography process related to TFT–LCD manufacturing. Typically, a negative-type photoresist consists of a polymer binder, polyfunctional monomer (or cross-linker), photo initiator, solvent, and additives. Therefore, the structure and characteristics of polymer binders and cross-linkers, intensity of the interpenetration network, and the proportions of the polymer binder affect the mechanical properties and the pattern profile of the photo spacers. In this article, we will discuss two topics. First, we will discuss the use of poly(methacrylic acid-co-styrene-co-glycidal methacrylate) as a polymer binder (ca. 15 wt%) in order to reveal the dependence of the mechanical properties of the photo spacers on the change in the ratio of DPHA from 7 to 13 wt%. Second, we will discuss the addition of different characteristics (including the soft segment of BuMA, hard segment of BzMA, and acrylic-silica sol) and proportions of an acrylic monomer (ca. 1–3 wt%) to the photoresist in order to bring to light the inflenuce of the mechanical properties and the profile of the patterns. The experimental data are listed in Table 1.

Effect of DPHA Content on Mechanical Behavior

Superior mechanical properties (elastic recovery = 80.7%, compression = 225 mN, surface hardness = 3H) of patterns were obtained by adding 7 wt% of DPHA to the photo spacers (Table 1). The photo spacers still maintained superior mechanical properties (elastic recovery = 80.5%, compression = 200 mN, surface hardness = 3H) when the amount of DPHA was increased to 8.5 wt%. Subsequently, the elastic recovery decreased to 72.0% when the amount of DPHA was further increased to 10 wt%. Then, the elastic recovery was maintained between 74.2 and 75.0% when the amount of DPHA was 11.5 and 13 wt%, respectively (Fig. 4). We concluded that the polymer binder comprised the hard segment of styrene and the thermal curing of the epoxy segment of glycidyl methacrylate (GMA), and the molecular weights were higher (approximately 13,000). On the other hand, the results showed that the superior mechanical properties when 7–8.5 wt% of DPHA was added to the photoresists were due to the superior characteristics of the polymer binders. However, the mechanical properties of the photo spacers were distored when the DPHA content was more than 8.5 wt% (the content of the polymer binder in the photoresists was relatively low).

Effect of Blending Monomers on Mechanical Behavior

One to 3 wt% of acrylic monomer (BuMA or BzMA or Pro-1264) was added to the photoresist and the amount of DPHA was kept fixed at 10 wt%. The results showed

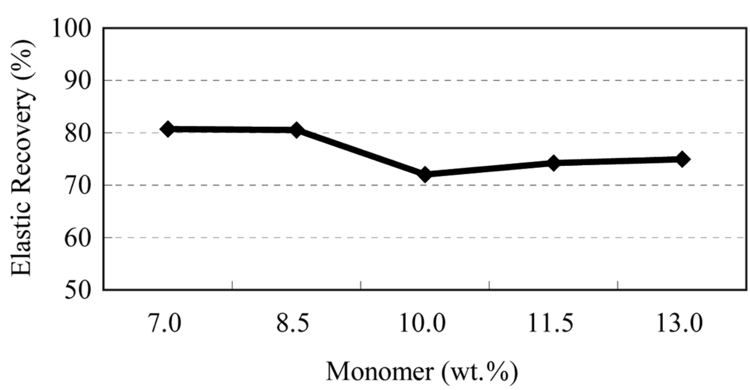

Figure 4. Effect of DPHA content on elastic recovery.

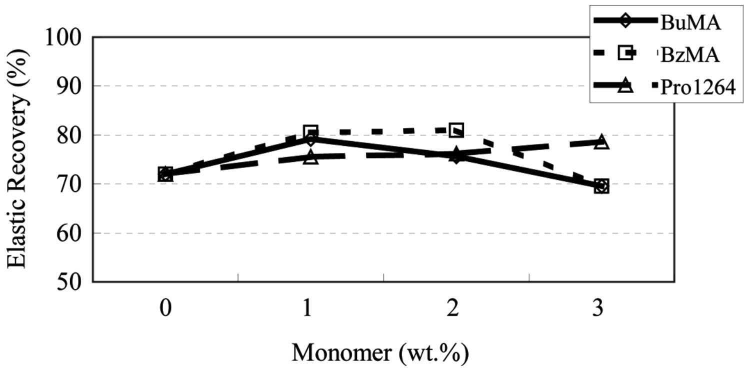

Figure 5. Effect of acrylic monomer content on elastic recovery.

that the elastic recoveries of patterns were 72.0, 79.2, 75.6, and 69.6%, and the amounts of BuMA added to the photoresists were 0, 1, 2, and 3 wt% (Fig. 5). Therefore, it appears that the superior elastic recovery of photo spacers can be obtained by introducing small amounts of BuMA (approximately 1–2 wt%) with softer characteristics of BuMA polymer (lower glass temperature, *Tg*), and cross-linkers such as DPHA with a high capacity for interpenetration into the photoresists. Subsequently, the elastic recovery of the photo spacers was distored when the monomer content of BuMA was 3 wt%, presumably because the proportion of the polymer binder was relative low in the photoresists. Similarly, the results showed the same trend when the BzMA monomer was added to the photoresists, but the BzMA monomer could still improve the elastic recovery when up to 2 wt% of this monomer was added because of the cyclic structure of BzMA polymer with higher *Tg* characteristics. Finally, the results showed that the addition of 1–3 wt% of Pro-1264 could improve the elastic recovery of patterns significantly. Therefore, it appears that the superior elastic recovery of patterns obtained by introducing small amounts of acrylic-silica sol of Pro-1264 having fine particles of silica (diameter of volume-average = 20 nm) offers a sufficiently large stereoscopic space to the photo spacers.

We investigated the effects of other mechanical properties (compression) of patterns while adding another 1–3 wt% of acrylic monomer (BuMA or BzMA or Pro-1264) and keeping the amount of DPHA fixed at 10 wt%. The results showed that the compression of the patterns was 200 mN when we added 1 wt% of BuMA in the photoresist. As previously stated, the compression of the patterns was slightly reduced to 175 mN when 2 wt% of BuMA was added in the photoresists because of the softer characteristics of BuMA with a lower *Tg* of the polymer (Fig. 6). This phenomenon can also be found in a BzMA system. The results showed that the original compression properties (200 mN) of the patterns were still maintained when up to 3 wt% of BzMA was added, presumably because of the rigid characteristics with a higher *Tg* of the BzMA polymer in the photo spacers. Finally, the results showed that the compression of patterns decreased to 175 mN when we added 1–3 wt% of Pro-1264 in the photoresists, presumably because of the poor combination of the fine particles of silica and the polymer. In summary, the compression of the patterns was kept at 200 mN when 1–3 wt% of BzMA was added in the photoresists. Therefore, the maintenance of good mechanical properties of the photo spacers can be attributed to the rigid characteristics of BzMA's structure.

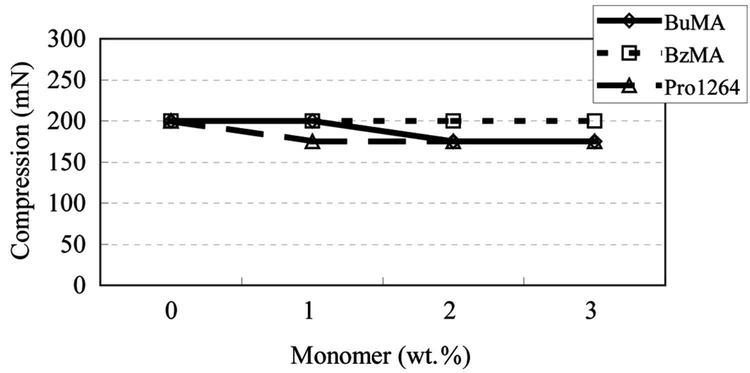

Figure 6. Effect of acrylic monomer content on compression.

The photoresist coating was applied on a glass substrate using a lithographic process. The thickness of the films was controlled between 4 and 5 µm, and then the surface hardness of films was measured. The results showed that the surface hardness of the films was maintained at 3H when we added 1–3 wt% of BuMA in the photoresists, and the surface hardness of films was enhanced to 4H when we added 2–3 wt% of BzMA or Pro-1264. Therefore, it appears that an excellent surface hardness of films can be obtained by introducing components such as BzMA (hard segment) and Pro-1264 that contain silica material in the photoresists (Fig. 7).

We concluded that the superior mechanical properties of photo spacers (elastic recovery, compression, and surface hardness) and the optimum recipes could be obtained by adding 2 wt% of acrylic monomers (BuMA or BzMA or Pro-1264) to the photoresists when the DPHA content was fixed at 10 wt%.

Effect of Pro-1264 Content on the Transmittance of Patterns

The photoresist coating was applied on a glass substrate using a lithographic process, and then the transmittance of patterns was measured while controlling

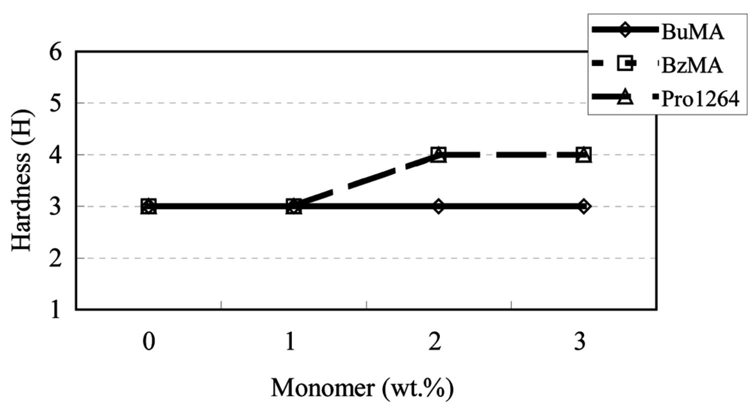

Figure 7. Effect of acrylic monomer content on surface hardness.

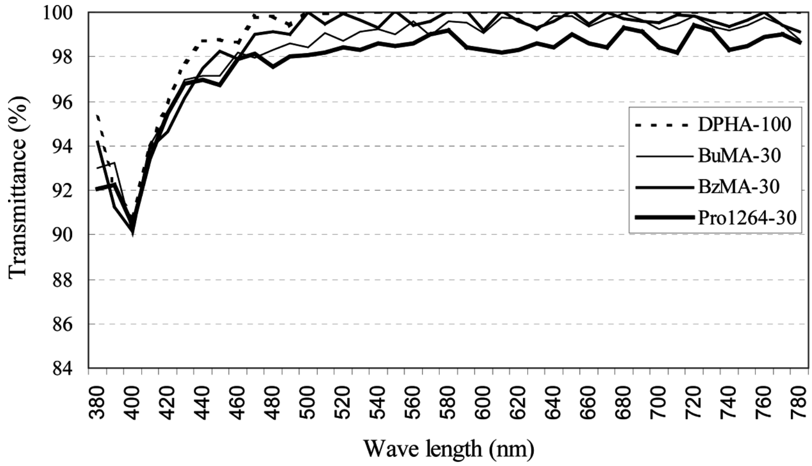

Figure 8. Effect of acrylic monomer content on transmittance of pattern.

the thickness between 4 and 5 μm. The transmittance of patterns was the main factor that affected the color saturation and brightness of the TFT–LCD's panel. The results showed that the transmittance (wavelength between 380 and 780 nm) of patterns could be reduced only by approximately 1% when we added 3 wt% of BuMA or BzMA monomer and the DPHA content was fixed at 10 wt%

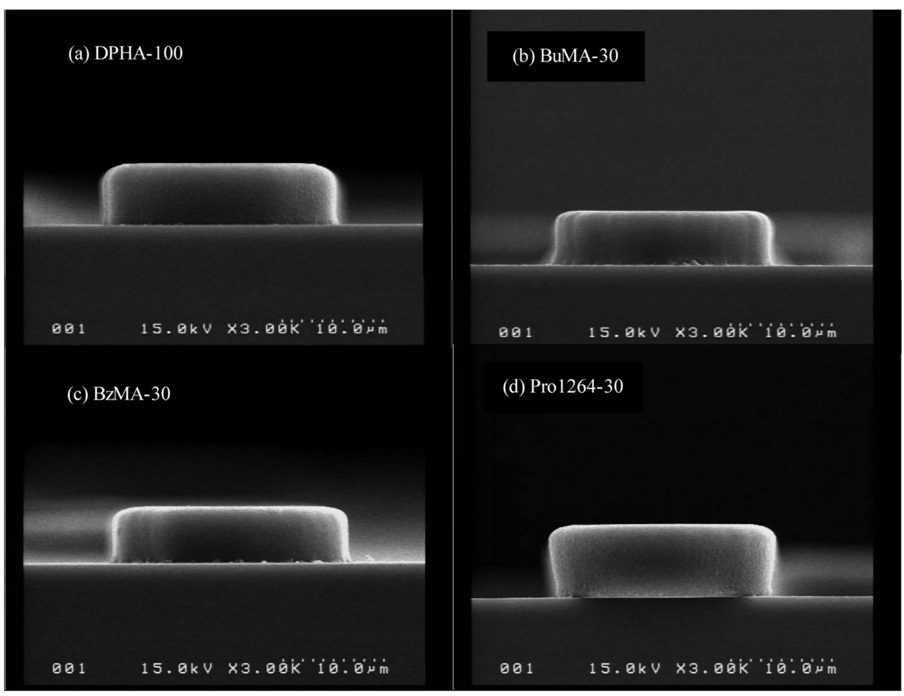

Figure 9. SEM diagrams of the photo spacers (a) DPHA-100; (b) BuMA-30; (c) BzMA-30; (d) Pro1264-30.

(Fig. 8). The results showed that the transmittance of patterns could be reduced by approximately 2% when we added 3 wt% of Pro-1264 because of the fine particles of silica from the acrylic-silica monomer in the photoresists. Further, the results satisfied the basic requirement of the TFT–LCD industry (transmittance of patterns: >95%).

Effect of Blending Monomer on the Profile of Patterns

Special geometric patterns of photo spacers are desired according to process requirements (such as the coverage of the alignment or liquid crystal) in TFT–LCD manufacturing. The photoresists coating was applied on a glass substrate using a lithographic process, and then the profiles of the photo spacers were observed by scanning electron microscope (SEM) images, as shown in Fig. 9. The results showed the vertical pattern of the photo space when we added 3 wt% of BuMA or BzMA monomer and the DPHA was fixed at 10 wt%. The photo spacers appeared to have an inverted conical pattern when we added 3 wt% of Pro-1264 in the photoresists because the transmittance of patterns worsened due to the low capacity of the interpenetration network.

Conclusions

A series of acrylic monomer (DPHA, BuMA, BzMA, and Pro-1264) was used as cross-linkers in negative-type photoresists. Subsequently, the mechanical properties and images of patterns were studied. The results showed that the superior mechanical properties (elastic recovery = 80.7%, compression = 225 mN, surface hardness = 3H) of patterns were obtained when 7 wt% of DPHA was added to the photo spacers. We concluded that the superior mechanical properties (elastic recovery, compression, and surface hardness) of patterns and the optimum recipes could be obtained by using 2 wt% of acrylic monomers (BuMA, BzMA, or Pro-1264) in the photoresists with the DPHA content fixed at 10 wt%. The photo spacer appeared to have an inverted conical pattern when we added 3 wt% of Pro-1264 in the photoresists because the transmittance of patterns worsened due to the low capacity of the interpenetration network.

References

[1] Kumano, A. (2001). *Journal of Photopolymer Science and Technology*, *14*, 23.
[2] Sabnis, R. W. (1999). *Displays*, *20*, 119.
[3] Sumino, T., & Inoue, A. (2004). "Photosensitive Resin Composition and Liquid Crystal Display Color Filter." U.S. Patent 6,680,763.
[4] Nakamura, K., & Sega, S. (2003). "High Photo-Sensitivity Curable Resin, Photo-Curable Resin Composition Production Method thereof, Color Filter and Liquid Crystal Display Panel," U.S. Patent 6,582,862.
[5] Ninomiya, A., & Yoshimura, H. (2003). *J. Appl. Polymer Sci.*, *87*, 684.
[6] Ahmad, S., & Zulfiqar, S. (2002). *Polymer Degrad. Stabil.*, *76*, 173.
[7] Cheng, T. S., Wu, M. H., Weng, W. S., & Chen, H. (2002). *Mater. Lett.*, *57*, 753.
[8] Lee, C. K., Don, T. M., Lai, W. C., Chen, C. C., & Lin, D. J. (2008). *Thin Solid Films*, *516*, 8399.

[9] Lee, C. K., Don, T. M., Lin, D. J., Chen, C. C., & Cheng, L. P. (2008). *J. Appl. Polymer Sci.*, *109*, 467.
[10] Diakoumakos, C. D., Raptis, I., Tserepi, A., & Argitis, P. (2002). *Polymer*, *43*, 1103.
[11] Chae, H. S., & Park, Y. H. (2007). *Mol. Cryst. Liq. Cryst.*, *463*, 203.
[12] Lin, D. J., Don, T. M., Chen, C. C., Lin, B. Y., Lee, C. K., & Cheng, L. P. (2008). *J. Appl. Polymer Sci.*, *107*, 1179.
[13] Hwang, S. T., Hahn, Y. B., Nahm, K. S., & Lee, Y. S. (2005). *Colloid. Surface. Physicochem. Eng. Aspect.*, *259*, 63.
[14] Yu, Y. Y., Chen, C. Y., & Chen, W. C. (2003). *Polymer*, *44*, 593.
[15] Koo, H. S., Chen, M., Kang, C. H., & Kawai, T. (2008). *Jpn. J. Appl. Phys.*, *47*, 4954.