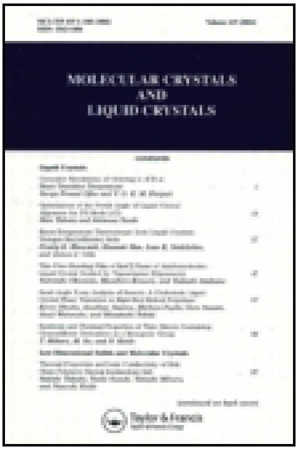

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HIGHLY TRANSPARENT AND THERMALLY STABLE PHOTOREACTIVE POLYMER

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HIGHLY TRANSPARENT AND THERMALLY STABLE PHOTOREACTIVE POLYMER

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New photoreactive prepolymers for the color filter resist of LCD were designed and synthesized through the reaction between several kinds of epoxy resins and methacrylic acid (MAA) or itaconic acid (ITA). The chemical structures of the prepolymers were confirmed by NMR and FT-IR spectroscopies. We investigated the photocure kinetics of the prepolymers using FT-IR spectroscopy, confirming high degree of photocuring of the prepolymers could be obtained upon UV irradiation. We also figured out the polymers possessed good thermal stability, showing little change of transmittance in the visible range even after heating at 250°C for 1 hour. The prepolymers showed good pattern resolution as low as several tens of microns.

Keywords: binder resin for color filter; high transparency; photocure kinetics; photoreactive prepolymer; thermal stability

1. INTRODUCTION

Recently, rapid progress of the information society has brought about boost in the needs on the flat panel displays, among which Liquid Crystal Display (LCD) is most widely used at present. Especially, in spite of the price, a market for Thin Film Transistor (TFT) LCD has dramatically increased because of its superior characteristics. Color filter is one of the most

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*Address correspondence to Jun Young Lee, School of Applied Chemistry and Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea, Tel.: 82-31-290-7319, Fax: 82-31-290-7330, E-mail: jylee7@skku.ac.kr important elements in the full color TFT-LCD and its performance greatly depends on the pixel formation technology. The pigment dispersion method, which is most widely used for TFT-LCD, may exhibit significant problems in reliability due to relatively poor thermal stability and transmittance of the photoreactive binder resin. Therefore, the photoreactive binder resin, which is a key material in the pixel formation process, should possess ease of process, high transparency and good thermal stability to improve performance of the color filter [1].

In this study, we designed and synthesized new photoreactive prepolymers bearing rigid cyclic moieties and photoreactive acrylic double bond. We expect that the rigid cyclic moieties and double bonds give rise to thermal stability and photoreactivity, respectively [2]. We, therefore, believe the prepolymers may be used for many potential applications and especially as a binder resin for the color filter resist of LCD [3,4]. We investigated photocure kinetics of the prepolymers using FT-IR spectroscopy [5–9] and thermal stability by monitoring the change in the transmittance of the polymer film upon heating. We also observed the pattern resolution of the prepolymer using SEM and the optical microscopy.

2. EXPERIMENTAL

Photoreactive prepolymers were synthesized by the reaction between two kinds of epoxy resins and methacrylic acid (MAA) or itaconic acid (ITA) as shown in Figure 1(a). The reaction was carried out using triphenyl phosphine or tetramethyl ammonium chloride as a catalyst in toluene or methyl ethyl ketone at 80°C. Figure 1(b) shows the chemical structures of the epoxy resins (YX4000H and EHPE3150) used in this study. The chemical structures of the prepolymers were confirmed by NMR and FT-IR spectroscopies. The photoreactive prepolymers were completely dissolved in the appropriate organic solvent such as methyl ethyl ketone, monochlorobenzene, toluene, or dimethylformamide with an appropriate photoinitiator. The solution was filtered through a membrane filter with a pore size of 0.5 μm and spin-coated on a glass substrate at 2000 rpm. The prepolymer film was then dried at 80℃ for 30 minutes, leading to a good quality of film with a thickness of about 1μm.

Photocuring of the prepolymer films were carried out by exposing them to UV light with the wavelength of 365 nm radiated from a high-pressure mercury lamp. Photocure behavior of the prepolymer films were quantitatively studied by monitoring change of absorbance at 810 cm^{-1} corresponding to $CH{=}CH_2$ double bond of MAA or ITA with the UV exposure time. The photocure conversions of the prepolymers were determined by normalization of the peak area of the double bond at 810 cm^{-1} with

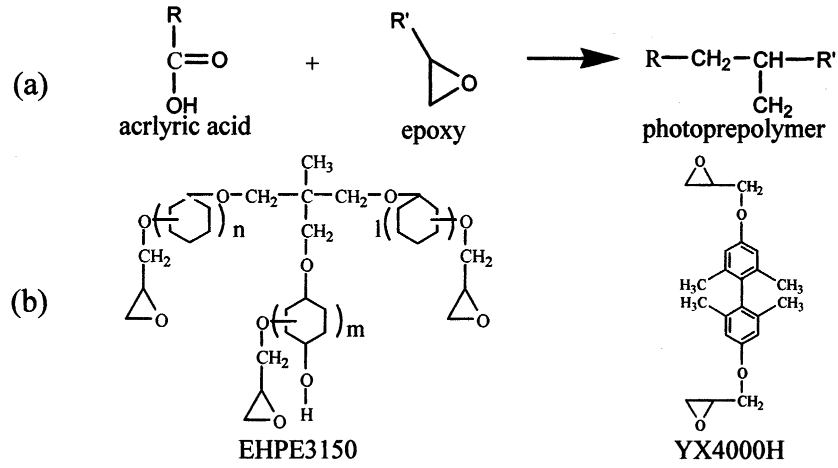

FIGURE 1 (a) Synthetic scheme of the photoreactive prepolymers. (b) Chemical structures of the epoxy reins.

respect to the peak area of C=O at 1720 cm^{-1} as a reference using the following equation.

$$\alpha_t = 1 - \left(\frac{A_{810}(t)/A_{1720}(t)}{A_{810}(0)/A_{1720}(0)}\right)$$

where, α_t is the photocure conversion of the prepolymer at the exposure time t, and $A_{810}(0)$, $A_{1720}(0)$, $A_{810}(t)$ and $A_{1720}(t)$ are the peak areas at the corresponding wavenumbers at the exposure time 0 and t, respectively. We used several kinds of the initiators as shown in Figure 3 in order to investigate the effect of the photoinitiator on the photocure behavior of the prepolymer. We also studied the effects of the photocure temperature and the UV intensity on the photocure behavior. The UV intensities, measured

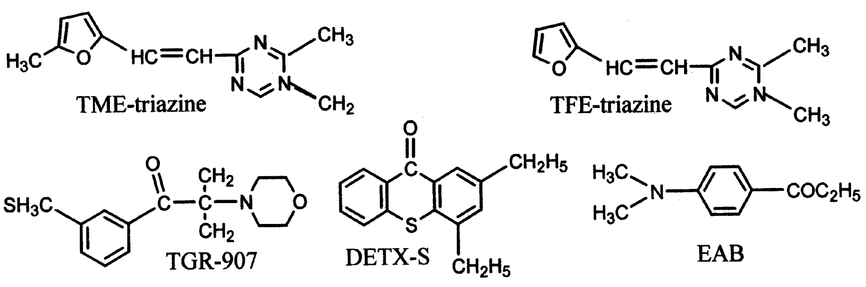

FIGURE 2 Chemical structures of the photoinitiators.

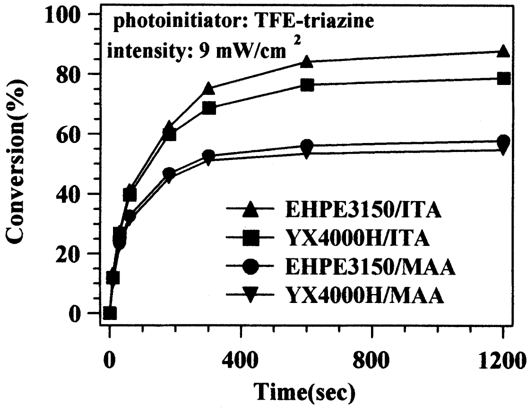

FIGURE 3 Photocure conversion of the prepolymers.

by the radiometry, were 5, 9, and 13 mW/cm^2 on the surface of the prepolymer film.

Surface morphology and the pattern resolution of the photocured film were observed using SEM and an optical microscopy. Microlithographic patterns were obtained from the prepolymers by exposing the prepolymer films to UV light through a photomask for 30 minutes and developing them in an appropriate solvent. We also studied thermal stability by observing change in the transmittance of the polymer film upon heating at 250℃ in atmosphere for 1 hour.

3. RESULTS AND DISCUSSION

We confirmed the chemical structures of the synthesized prepolymers by FT-IR and NMR spectroscopies. In the FT-IR spectra of the prepolymers, new characteristic absorption peaks were observed at 3200 ~ 3500 cm^{-1} (hydroxyl group), 1720 cm^{-1} (carbonyl group), and 810 cm^{-1} (acrylate double bond). In the NMR spectra of the prepolymers, the peak at 2.7–2.9 ppm corresponding the epoxide ring proton disappeared and new peaks at 5.6 and 6.1 ppm corresponding to the proton of the double bond appeared. These spectral results confirmed the syntheses of the prepolymers with the desired chemical structures.

We investigated the photocure behavior of the prepolymers by monitoring the change of the absorbance at 810 cm^{-1} relating to $CH{=}CH_2$ twisting vibration of the prepolymers with the UV exposure time. We figured out the absorbance at 810 cm^{-1} of all prepolymers decreased with the UV exposure time, confirming the photocuring took place in all prepolymer synthesized in this study. Figure 3 shows the change of the photocure conversion of the prepolymers with the UV (9 mW/cm^2) exposure time. As shown in Figure 3, the photocure conversions of the prepolymers increased extremely rapidly during the early radiation period and then slowly increased with exposure period. This implies the photocuring reaction takes place very extensively in the early stage to a high degree of conversion. The photocuring reaction seems to come to an end within 10 minutes since little change of the conversion was observed after 10 minutes. We also observed the photocure conversion increased with the radiation intensity and the photocure temperature.

Nevertheless, we observed the final photocure conversion of the prepolymer was strongly dependent on the structure of the prepolymer. As shown in Figure 3, the prepolymers bearing ITA moiety as the photoreactive group showed much higher conversion than those bearing MAA moiety. The final degree of conversion of EHPE3150/ITA and YX4000H/ITA was close to about 80% at 1200 seconds exposure, while the final conversion of EHPE3150/MAA and YX4000H/MAA reached only about 55%. We consider the difference in the final conversions must result from the difference in the steric hindrance and the reactivity between MAA and ITA moiety in the prepolymers. We also observed the structure of the photoinitiator plays an important role on photocuring reaction of the prepolymers as shown in Figure 4, showing TFE-triazine gave rise to the highest conversion. TFE-triazine gave rise to the highest conversion of about 80%, while TRG-907/DETX-S/EAB resulted in the lowest conversion of about 50%.

We observed the surface morphology of the photocured YX4000H/ITA, the film surface was extremely smooth. We also observed the pattern

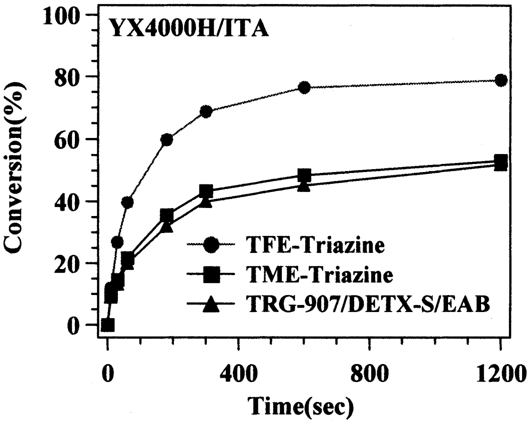

FIGURE 4 Photocure conversion of YX4000H/ITA initiated by various photoinitiators.

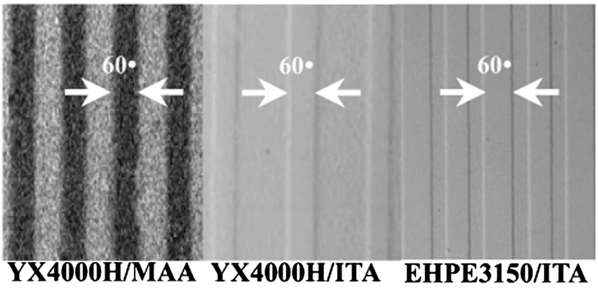

FIGURE 5 Photolithographic pattern. (a)YX-4000H/MAA, (b)YX-4000H/ITA, (c) EHPE3150/ITA.

morphologies obtained from the prepolymers. As shown in Figure 5, we figured out the prepolymers bearing ITA (EHPE3150/ITA and YX4000H/ITA) produced better lithographic patterns than the prepolymers bearing MAA (EHPE3150/MMA and YX4000H/MAA) did. We believe the better photolithographic patterns of the prepolymers prepared with ITA must be due to not only the higher degree of the conversion but also existence of the free acid group in the prepolymer. We could successfully obtain a good lithographic pattern with a resolution of several tens of microns. As shown in Figure 6, the photocured films showed little change of transmittance in

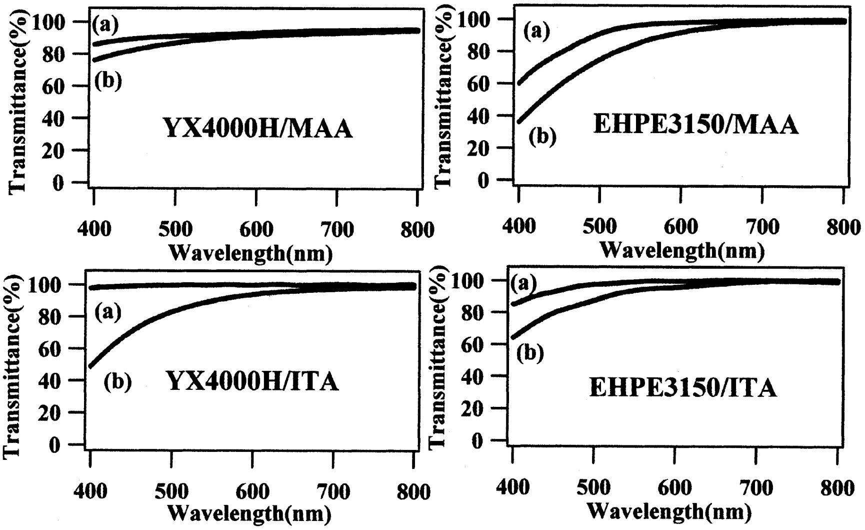

FIGURE 6 UV-vis spectra of the photocured polymer films. (a) before heating (b) after heating at 250°C for 1 hour.

the visible region even after heating at 250℃ for 1 hour compared with the transmittance of the unheated photocured film. We, therefore, suggest the photoreactive prepolymers synthesized in this study can be used as a binder resin for the color filter resist of LCD.

4. CONCLUSIONS

We designed and synthesized new photoreactive acrylate prepolymers by the reaction between two kinds of the epoxy resins and MAA or ITA, which were expected to possess good thermal stability as well as photoreactivity. We confirmed the desired chemical structures of the prepolymers from NMR and FT-IR spectroscopies. We studied the photocure behaviors of the photopolymers by monitoring the absorbance change at $810\,\mathrm{cm}^{-1}$ of FT-IR spectra, confirming photocuring of the prepolymers to high degree of conversion upon irradiation for less than 10 minutes. We found the photopolymers prepared with ITA showed much higher photocure conversion and better lithographic pattern resolution than those prepared with MAA. The photocured films exhibited fairly good thermal stability. We, therefore, conclude the prepolymers synthesized in this study can be applied to a binder resin for the color filter resist.

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