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Thermally Stable Photoreactive Polymers as a Color Filter Resist Bearing Acrylate and Cinnamate Double Bonds

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Abstract: Photoreactive polymers as a color filter resist containing both photoreactive acrylate and cinnamate double bonds were synthesized usin two step reactions. The chemical structures of the synthesized polymers were confirmed by ^{1}H-NMR and FT-IR spectroscopy. The photoreactive polymers were quite soluble in most common organic solvents and produced excellent quality thin films by spin-coating. The photocuring kinetics of the acrylate and cinnamate double bonds were examined by FT-IR and UV-Vis spectroscopy, which confirmed the excellent photoreactivity of both the acrylate and cinnamate double bonds in the polymers. Upon UV irradiation, photocuring was almost completed within approximately 5 min, irrespective of the type of the prepolymers. The polymers also exhibited superior thermal stability, showing little change in transmittance in the visible region even after heating to 250 °C for one hour. Photolithographic micropatterns could be obtained with a resolution of a few microns.

Keywords: photoreactive polymer, photocure kinetics, photolithographic micropattern, thermal stability, optical transmittance.

Introduction

Recently, there have been many researches in the area of synthesis and application of polymers bearing photosensitive groups.[1-6] The photoreactive polymers have found various applications in the field of microlithography including integrated circuit technology, printing technology, and liquid crystal display. The polymers having α,β-unsaturated carbonyl groups either in the backbone or in the pendant groups undergo crosslinking upon irradiation with UV light or an electron beam and such polymers are regarded as the negative photoresists. To be used as commercial negative photoresist materials, polymers should possess good solubility, ability to form films, high photosensitivity, and thermal stability.

The most glamorous application of color filter is in full-color flat panel displays such as computer and TV monitors. Color filter should possess superior thermal, chemical, and light stability. The pigment dispersion method, which is mainly used for TFT-LCD, contains relatively complicated process and may exhibit poor thermal stability. The pigment-dispersed color filter must show little change in transparency after heated at 250 °C for about one hour, at which the liquid crystal alignment layer is formed.[7-9]

In this study, we designed and synthesized new photoreactive prepolymers bearing both thermally stable cyclic and photoreactive moieties. The photoreactive prepolymers are expected to produce the photolithographic pattern with high transmittance and good thermal stability.[10,11] We investigated photocuring kinetics of the prepolymers using FT-IR and UV-Vis spectroscopies. We evaluated thermal stability of the photocured polymer film through observation of changes in the transmittances of the polymer film upon heating. We also observed the photographic micropattern resolution using optical microscopy.

Experimental

Polymers as the color filter resists containing both cyclic moieties and photoreactive groups were synthesized through

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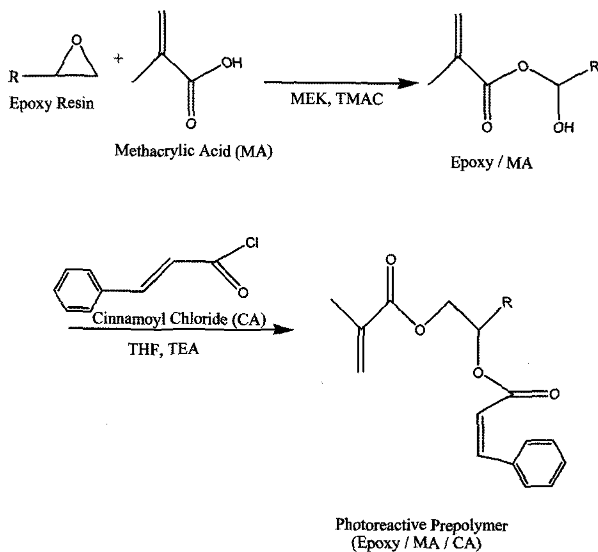

Figure 1. Syntheic scheme of the photoreactive prepolymer.

two steps. Figure 1 shows the typical reaction scheme of the photoreactive polymer. In the first step, epoxy/methacrylate (Epoxy/MA) was prepared by the reaction between epoxy resin and methacrylic acid.[12] Four kinds of commercially available epoxy resins (Nippon Kayaku Co. Ltd.) were used in this study, whose chemical structures are shown in Figure 2. The reaction was carried out using tetramethyl ammonium chloride (TMAC) as a catalyst in the methyl ethyl ketone (MEK) at 75 °C for 120 h. In the second step, cinnamate double bond was incorporated into epoxy/MA prepolymer by the reaction between hydroxyl group of epoxy/MA and cinnamoyl chloride, producing epoxy/MA/CA. The reaction was carried out using triethylamine as a catalyst in THF at room temperature for 12 h. The chemical structures of the photoreactive prepolymers were confirmed by ^{1}H-NMR and FT-IR spectroscopies.

The photoreactive prepolymers were completely dissolved in the organic solvent such as MEK, monochlorobenzene, toluene, or DMF. The solution was filtered through a membrane filter with a pore size of 0.5 μm and spin-coated on a glass substrate at 2,000 rpm for 80 sec using spinner. The photoreactive prepolymer film was then dried at 70 °C for 20 min, leading to an excellent quality of film with a thickness of about 1 μm. Photocuring was carried out by exposing prepolymer films to 254 nm UV light with intensity of 25 mW/cm^2 on the surface of the film.

When acrylates are photopolymerized by irradiation with short-wavelength UV light, it has been suggested that the absorption of light produces an excited triplet state which may be regarded as a diradical ($\cdot CH_2{=}C\cdot(H)R$). The diradical attacks monomer and then produces two monoradicals which initiate polymerization.[13,14] Photocuring behaviors of the acrylate double bonds were investigated by monitoring the absorbance change at 810 cm^{-1} of FT-IR spectra corresponding to the C=C twisting vibration of the acrylate groups.[15,16] The photocure conversion of the acrylate double bond was determined by normalization of the peak area at 810 cm^{-1} with 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 acrylate double bond 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.

Since photocuring of the cinnamate group does not produce significant peak change in the FT-IR spectra, photocuring behaviors of the cinnamate double bonds were studied by monitoring the absorbance changes at 275 nm of UV-Vis spectra of corresponding cinnamate double bonds. We also studied thermal stability by observing transmittance changes of the photocured polymer film upon heating at 250 °C for 1 h using TGA (Hi-Res TGA2950 TA Instruments).

Photolithographic micropatterns were prepared by exposing the photoreactive prepolymer films spin coated on the glass substrate to UV light through a quartz photomask for 10 min and developing them in an appropriate solvent. The residual negative image was then treated at 70 °C for 10 min. The micropattern resolutions were observed using optical microscopy.

Results and Discussion

We confirmed the chemical structures of the synthesized prepolymers by ^{1}H-NMR and FT-IR spectroscopies. In the ^{1}H-NMR spectra of the epoxy/MA prepolymers, the peak at

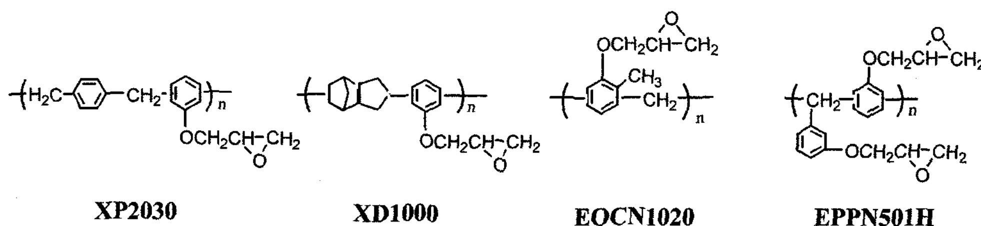

Figure 2. Chemical structures of epoxy resins.

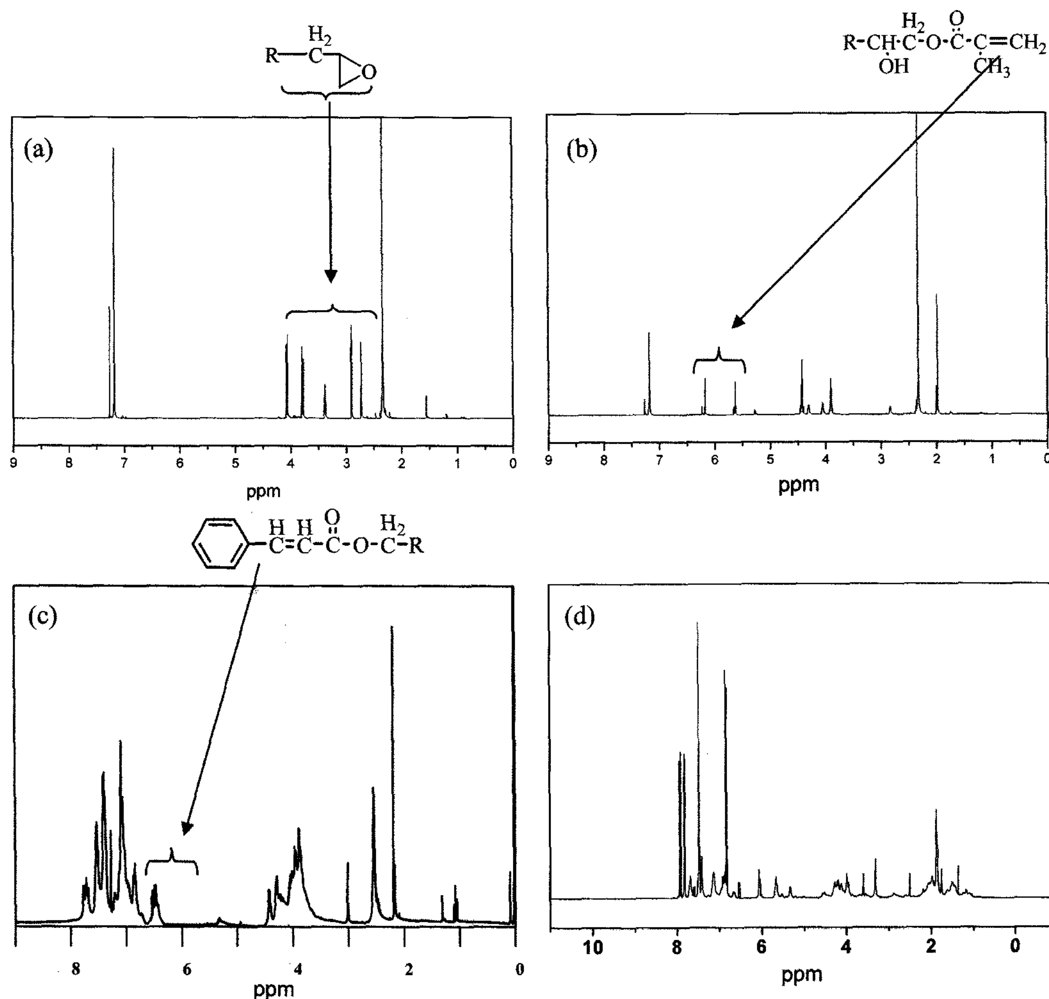

Figure 3. ^{1}H-NMR spectra of (a) epoxy, (b) epoxy/MA, (c) epoxy/CA, and (d) XP2030/MA/CA.

2.7-2.9 ppm corresponding to the epoxide ring proton disappeared and new peaks at 5.6 and 6.1 ppm corresponding to the proton of the double bond appeared. Figure 3 shows the ^{1}H-NMR spectra of (a) epoxy, (b) epoxy/MA, (c) epoxy/CA, and (d) XP2030/MA/CA. In the FT-IR spectra of the epoxy/MA 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). These spectral results confirmed the syntheses of the epoxy/MA with the expected chemical structures.

We found the epoxy/MA prepolymers were only partially soluble in most of organic solvents, possibly because of hydrophilic nature as well as strong hydrogen bonding of hydroxyl groups of epoxy/MA prepolymers. However, the solubility of epoxy/MA/CA prepolymers was revolutionarily improved, becoming completely soluble in most of organic solvents. The improved solubility must result from weakening of hydrogen bonding of hydroxyl groups, which reacted with cinnamoyl chloride to form the cinnamate.

We confirmed very effective photocuring of the acrylate double bond in epoxy/MA/CA prepolymers as shown in Figure 4. The absorption peak at 810 cm^{-1} corresponding to acrylate C=C bond decreased with UV irradiation time as shown in Figure 4(a). We also figured out photocuring of the acrylate double bond took place extremely fast. Figure 4(b) shows the photocure conversion obtained from the normalized absorbance of the peak at 810 cm^{-1} with respect to the absorbance of carbonyl peak at 1720 cm^{-1} as a standard. For four prepolymers, conversion rapidly increased within the initial 120 s, and thereafter gradually proceeded, even though a little difference in the reaction rate and the final conversion were observed. Photocure conversions of EPPN501H/MA/CA and XP2030/MA/CA reached 93% and 85% after 1200 s. Also, photocure conversions of EOCN1020/MA/CA and XD1000/MA/CA reached 94.2% and 86% after 1200 s, respectively. We believe the differences in the reaction rate and the conversion must result from the different steric hindrance and the concentration of the acrylate double bonds.

We also confirmed the effective photocure of the cin-

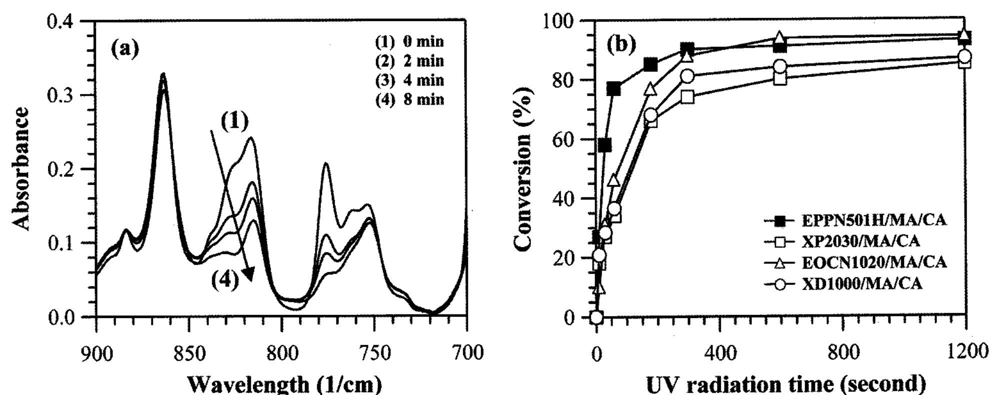

Figure 4. (a) FT-IR spectra and (b) photocure conversions of the acrylate double bond with UV exposure time.

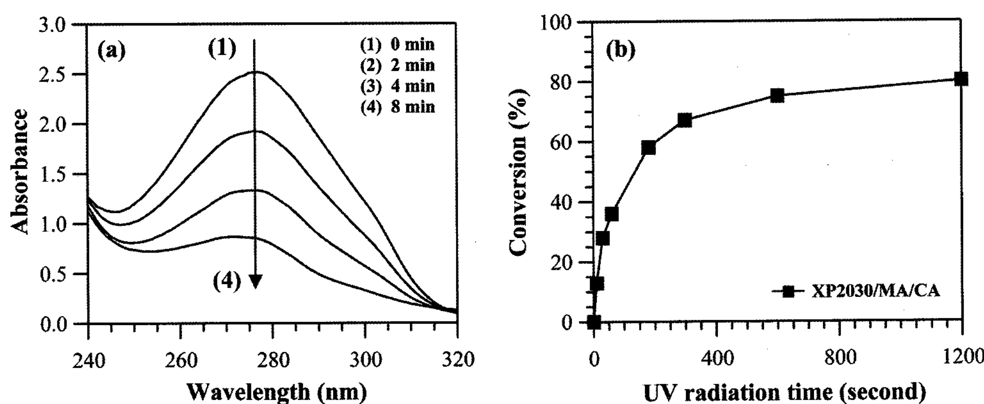

Figure 5. (a) UV-visible absorption spectra and (b) photocure conversion of the cinnamate double bond with UV exposure time.

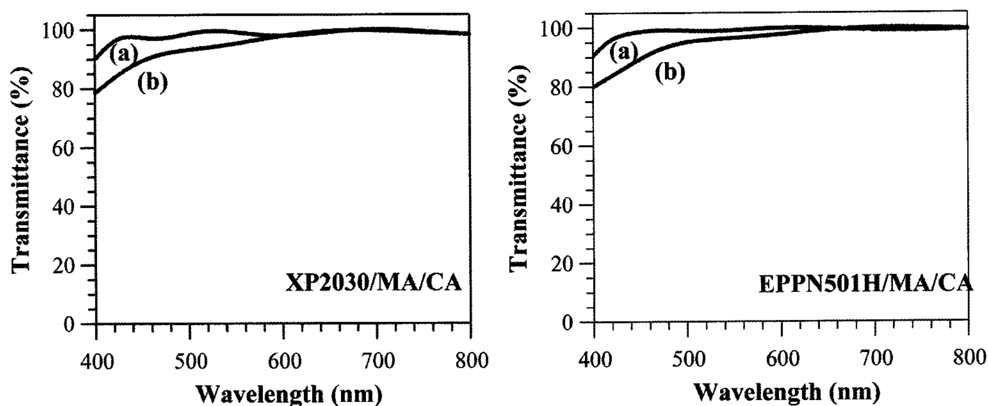

Figure 6. TGA curves of the photocured polymer films (a) unheated (b) heated at 250 °C for 1 h.

namate double bond in XP2030/MA/CA as shown in Figure 5 as already reported before.[17] The absorption peak at 275 nm corresponding to cinnamate double bond decreased upon UV irradiation as shown in Figure 5(a), indicating photodimerization of the cinnamate double bonds. It is interesting that the photocure of the cinnamate double bond took place as fast as that of acrylate double bond did. Figure 5(b) shows the photocure conversion of the cinnamate double bond in XP2030/MA/CA with UV irradiation time, exhibiting steep increase of the photocure conversion during the initial UV irradiation period. The conversion finally reached 80% after 1200 s.

As shown in Figure 6, the photocured film of prepolymers, XP2030/MA/CA and EPPN501H/MA/CA, showed

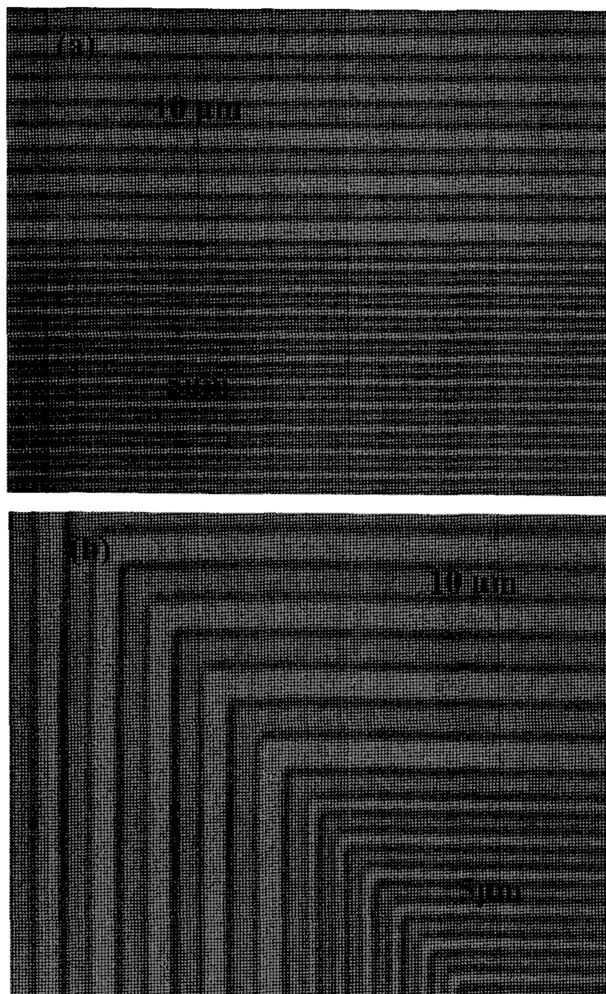

Figure 7. Photolithographic pattern of the photoreactive polymer.

little change of the transmittances in the visible region even after heating at 250 °C for 1 h compared with those of the unheated photocured film, implying fairly good thermal stability. Using TGA instrument, thermal decomposition temperature of XP2030/MA/CA, EPPN501H/MA/CA, XD1000/MA/CA and EOCN1020/MA/CA were observed at 400, 300, 350, and 360 °C, respectively.

We found the prepolymers synthesized in this study formed excellent lithographic patterns as shown in Figure 7. We could successfully obtain a good photolithographic pattern with resolution of as low as 5 μm. We consider the photoreactive prepolymers synthesized with high transmittance and thermal stability in this study can be applied to photoreactive materials of the display technology.

Conclusions

We designed and synthesized new photoreactive prepolymers, whose chemical structures were confirmed by ^{1}H-NMR and FT-IR spectroscopies. The solubility of new photoreactive prepolymers were revolutionarily improved, becoming completely soluble in most of organic solvents. We studied the photocure kinetics by FT-IR and UV-Vis spectroscopies, confirming the extremely high photoreactivity of the prepolymers. The polymers possessed good thermal stability, showing little change of the transmittances in the visible region even after heating at 250 °C for 1 h compared with those of the unheated photocured polymers. We could successfully obtain excellent photolithographic patterns with the resolution of as low as five microns. We, therefore, consider the photoreactive prepolymers synthesized with high transmittance and thermal stability in this study can be applied to many applications including photoreactive materials of the display technology.

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