Visible Laser Recordable Photopolymer Based on Poly(*p*-hydroxystyrene) and Acidolysis of Crosslinked Vinyl Ether

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Positive-working photoresists based on poly(*p*-hydroxystyrene) (PHS), 2,2-bis[4-(2-(vinylloxy)ethoxy)phenyl] propane (BPA-DEVE) has been investigated on their sensitivities to 488-nm argon ion laser using binary acid generated system. 2-(2',4'-dimethoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (TAZ114), diphenyliodonium *p*-toluenesulfonate (DITS) and diphenyliodonium trifluoromethanesulfonate (DITFMS) were used as photoacid generator. Acridine orange, rose bengal, thioxanten-9-one and 3,3'-carbonylbis(7,7'-diethylaminocoumarin) (KCD) were used as sensitizing dye. In these photopolymers, the polymer containing of TAZ114 and acridine orange exhibits the highest sensitivity to 488-nm light at 147.5 mJ/cm².

Keywords: Visible laser recordable, Poly(*p*-hydroxystyrene), Vinyl ether crosslinker, De-crosslinking

1. Introduction

With the development of laser technology and imaging, one of the research fields has been focused on visible sensitive photopolymers for application to photo-imaging, holography, plate making by "computer to plate" prepress system and so on. With regard to initiation step, the main problem is to define photosensitive system, whose absorption spectra match the laser emission wavelength. In the visible lights, photoinitiation is induced through two different processes: (a) Direct absorption of light by photosensitive system; (b) Sensitized formation of initiating system. The sensitizing dye absorbs the light and then transfers its excitation energy to the photoinitiator. In both cases, the reactivity in the excited states will govern the efficiency of the photosensitive systems. [1,2]

From this concept, the negative and positive-working photoresists sensitive to visible light have been developed. Hotta et al. [3] reported that the negative-working photoresist consisting of PHS and hexamethoxy methylmelamine crosslinker and photoacid generator (PAG), which is high sensitivity to 488-nm argon ion laser light based on

cationic polycondensation. Ohe et al. [4] reported the positive-working photoresist consisting of poly(tetrahydropyranyl methacrylates) activated by dye-sensitized decomposition of diphenyliodonium salt with high sensitivity.

It is well-known that three-component photopolymers containing of base polymer which has hydroxy group, PAG, and vinyl ether crosslinker have either positive or negative working behavior with high sensitivity and good pattern, depending on process condition. [5,6] At high temperature of prebake, the vinyl ether groups react with the hydroxy groups to form acetal crosslinked networks. After post exposure bake (PEB), these networks are acid-catalytically de-crosslinked via protonation by photogenerated acids and subsequent hydrolysis to give alcohol and aldehyde. Under these conditions, the photopolymer exhibits the positive working behavior. When the concentration of PAG is very lower than vinyl ether crosslinker, the photopolymer exhibits negative working behavior because of the cationic polymerization of vinyl ether groups.

In our study, visible light sensitive

photopolymers consisting of PHS and vinyl ether crosslinker were prepared and investigated their sensitivities.

2. Experimental

2.1. Materials

PHS was commercially available ($\overline{M}_w = 2.1 \times 10^4$, $\overline{M}_w/\overline{M}_n = 1.1$). DITS was synthesized according to the literature [7] BPA-DEVE was synthesized according to the literature. [8,9] TAZ114 was purchased from Midori Chemistry. Thioxanthan-9-one and DITFMS were commercially available from Aldrich and Kasei Chemical Industries, Ltd., respectively. Acridine orange and rose bengal were purchased from Wako Chemicals.

2.2. Measurements

UV-Visible spectra were recorded on a Hitachi U-3000 spectrophotometer. The photosensitive film thicknesses were measured with a Tencor Alphastep 200.

2.3. Sensitivity measurement

To a 21.5 wt% solution of PHS in diethylene glycol dimethyl ether was added BPA-DEVE, sensitizing dye and PAG. The weight ratio of PHS: BPA-DEVE: sensitizing dye was 100: 17: 1.5. The photopolymer solution was coated on a silicon wafer by spin coating and prebaked at 120°C for 15 min. The film was exposed to an argon ion laser at 488 nm through a step tablet (Kodak No 2). After exposure, the film was baked at 120°C for 10 min and then developed in a 2.38 wt% aqueous solution of tetramethylammonium hydroxide (TMAH) for 1 min. The characteristic curves were obtained by plotting the normalized film thickness against the exposure energy.

3. Results and Discussion

3.1 Photosensitivity

The polymer films consisting of four components were prepared and investigated their sensitivities by varying sensitizing dye, as shown in Table 1.

Table 1. Absorption properties of dyes in acetonitrile.

Dye	$\lambda_{\max}$ (nm)	$\epsilon_{\lambda_{\max}}$	$\epsilon_{488 \text{ nm}}$
 Rose bengal	558	10,300	566
 Thioxanthan-9-one	378	5,900	12
 KCD	456.5	355,000	65,800
 Acridine orange	494	48,400	44,898

The sensitivities of these polymers were summarized in Table 2.

Since the sensitivity in this system involves the de-crosslinking at exposed areas with presence of

Table 2. The sensitivity values of photopolymer prepared in this study

PAG	Sensitizing dye	Sensitivity (mJ/cm ²)
TAZ114 (7 w%) (5 w%)	KCD	922
	KCD	591
	thioxanten-9-one	2,066
	rose bengal	7,524
	acridine orange	147
DITS (7 w%) (5 w%)	KCD	> 4,536
	KCD	> 7,776
	acridine orange	> 8,145
DITFMS	KCD	> 8,460

generated acid, therefore, the sensitivity depends on the amount of acid and properties, acid strength and molecular size. [10] The mechanism of de-crosslinking was shown in Scheme 1.

Scheme 1. The mechanism of crosslinking and de-crosslinking.

From Table 2, it is showed that TAZ114 give the higher sensitivity than DITS and DITFMS, when they were used as PAG. Because generated HCl from TAZ114 is stronger and smaller acid than trifluoromethanesulfonic acid and *p*-toluenesulfonic acid, which were generated from DITFMS and DITS, respectively. Another reason is that TAZ114 has 6 chlorine atoms in each molecule, which makes it possible to generate a larger number of acidic species than DITS and DITFMS. [3]

The mechanism of acid generation of TAZ114, was shown in Scheme 2. [3]

Scheme 2. The mechanism of acid generation.

For the reaction mechanism between sensitizing dyes and TAZ114, DITS and DITFMS, we consider that it was electron transfer reaction as several reports. [1-4]

When TAZ114 is used as PAG, the relative order of sensitization of the sensitizing dye was acridine orange > KCD > thioxanthen-9-one > rose bengal. However, there is a disadvantage that acridine orange reacts with TAZ114 in dark.

3.2. Concentration of PAG

The increase of concentration of DITS from 5 wt% to 7 wt% exhibits the increase of sensitivity. It indicates that the sensitivity increase due to the higher concentration of generated acid from DITS. Interestingly, the increase of TAZ114 content exhibits the decrease sensitivity. This result may be due to the mechanism of acid generation. In the case of TAZ114, HCl is generated from chlorine radical. When the concentration of chlorine radical is too high, the side reaction of free radical occur and effect on decrease of the amount of generated acid.

3.3. Contrast

The contrast behavior of TAZ114 with varying sensitizing dyes in photopolymer is shown in Figure 1. From Figure 1, the similarity in contrast values, >10, is observed. Because the contrast behavior depends on the structure of generated acid. [10] Therefore the same generated acid, HCl, give the similar values.

Figure 1. The characteristic curves of TAZ114.

4. Conclusion

The positive-working photoresists based on

PHS, BPA-DEVE and PAG was developed, having sensitivity with an argon ion laser by using sensitizing dye. The photopolymer containing TAZ114 and acridine orange required exposure energy with 488-nm light about 147 mJ/cm² to complete dissolution of exposed areas.

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