PREPARATION OF CHEMICALLY AMPLIFIED PHOTORESISTS WITH N-HYDROXYPHthalIMIDE STYRENESULFONATE GROUPS AND THEIR PROPERTIES

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Chemically amplified photoresists are known to be a resist material highly sensitive and of high resolution. They are the most promising material for the production of advanced microelectronic devices. A chemically amplified photoresist system consists of a photoacid generator and a t-butyloxycarbonyl(t-BOC) blocked polymer matrix. Commonly used photoacid generators are derivatives of onium salts. Some UV deblockable latent sulfonic acid derivatives have also been developed.¹⁻³

It is known that N-hydroxyphthalimide sulfonate(HPS), one of the latent sulfonic acid derivatives, generates sulfonic acid upon exposure to 254nm UV light. It was used as a photoacid generator for chemically amplified photoresists,⁴ an initiator for photo-crosslinking of PGMA,⁵ or a catalyst for acid-curable coatings.⁶ Photolysis of HPS derivatives leads to homolytic cleavage of an N-O bond resulting in radical pair of a phthalimidyl radical and a sulfonyl radical. The pair can undergo solvent cage escape followed by the formation of sulfonic acid and N-hydroxyphthalimide through hydrogen abstraction.

Applying the photochemical reaction that HPS photodecompose to produce sulfonic acid, a chemically amplified photoresist with HPS groups in the main chain was prepared. Changes in the physical properties of the photoresist upon irradiation were studied. 4-t-Butyloxycarbonyloxyphenyl methacrylate

Scheme 1

(THPM), a t-BOC-blocked monomer was prepared according to reported procedure.⁷ N-Hydroxyphthalimide styrenesulfonate(PSS), a comonomer having HPS group, was prepared by reacting styrenesulfonyl chloride and N-hydroxyphthalimide. P(THPM-co-PSS), a chemically amplified photoresist with HPS groups, was prepared by copolymerizing of THPM and PSS after double precipitation in ethyl ether.

Table I summarizes the preparation condition and physical properties of copolymers. Specific viscosities of these polymers are around 0.1 dl/g. Yields lie between 60 and 80%. Thermal analysis of these copolymers indicates that decomposition temperature of t-BOC group is 170-180°C and that of the polymers is around 280°C.

UV absorption spectra of the polymer C-1 film upon irradiation of 254nm

Scheme 2

Table I. Preparation Condition^a and Physical Properties of P(THPM-co-PSS)

Polymer	THPM (g)	PSS (g)	DMF (ml)	Yield (%)	η_{sp}/C^b (dl/g)
C-0	1.0	0	5	64	0.106
C-1	1.0	0.1	5	69	0.097
C-2	0.7	0.3	5	78	0.096
C-3	0.5	0.5	5	70	0.094

a : Concentration of AIBN : 0.05mol/L

b : [c] = 0.5g/dL , solvent : DMF, 25°C

UV light showed isosbestic points at 207, 224, and 247nm. The absorbance below 250nm increased with irradiation. It seems to be due to the formation of photo-Fries rearrangement product of THPM units and/or that of photodecomposition product of PSS units. IR difference spectrum of polymer C between before and after irradiation showed the increase in the absorption bands around 3400cm^{-1} and 1720cm^{-1} . It indicates the production of a $-\text{SO}_3\text{H}$ group in a PSS unit and the formation of a ketone group by photo-Fries rearrangement of THPM unit respectively. The decreases in the absorption band at 1800cm^{-1} and 1770cm^{-1} indicate the photodecomposition of $\text{C}=\text{O}$ group in a PSS unit and a carbonate $\text{C}=\text{O}$ group in a THPM unit. These results imply that photochemical reaction took place in both of THPM and PSS units upon irradiation of 254nm UV light.

The change of insoluble fraction of the copolymer C in various solvents between before and after irradiation was studied. The copolymer was coated on a quartz plate. Insoluble fraction of the polymer films after irradiation was determined from the difference between absorbance at the isosbestic point of the UV spectra before and after dipping the quartz plate in various solvents for a given time at room temperature.

No copolymer C was not soluble in the buffer solutions at pH values between 4 and 11. However, the solubility increased with pH value increases and irradiation time. Fig 1 shows the change in the insoluble fraction of copolymer C as a function of irradiation time at pH 11. While solubility of polymer C-0, a homopolymer of THPM, is not affected by irradiation, that of copolymer C increases with irradiation time and amount of PSS units in the copolymer.

The changes in the insoluble fraction of copolymer C in organic solvents was also studied. Fig. 2 shows the insoluble fraction of copolymer C in n-propanol

as a function of irradiation time. Before irradiation, the polymer films are not soluble in n-propanol. However, the solubility increases with irradiation time and increasing the amount of PSS unit in the copolymer. Fig. 3 shows insoluble fraction of copolymer C in chloroform as a function of irradiation time. Before irradiation the polymer films were soluble in chloroform. However, they become insoluble after irradiation. The insoluble fraction

Fig 1. Insoluble fraction of copolymer C-1(○), C-2(●), and C-3(▽) as a function of irradiation time at pH 11.

Fig. 2. Insoluble fraction of copolymer C-1 (○), C-2 (●), and C-3 (▽) as a function of irradiation time in n-PrOH.

Fig. 3. Insoluble fraction of copolymer C-1 (○), C-2 (●), and C-3 (▽) as a function of irradiation time in chloroform.

increased with irradiation time and increasing the PSS unit in the copolymer.

The above results shows that copolymer C has properties of a dual-tone photoresist which becomes soluble in alkaline or polar solvents such as n-propanol upon irradiation but insoluble in nonpolar organic solvents such as chloroform. The results can be explained by the formation of sulfonic acid and phenolic -OH groups in the polymer chain during irradiation which makes the copolymer to have polar properties.

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References

1. G. Berner, R. Kirchmayr, G. Rist, and W. Rutsch, *J. Rad. Curing*, **13**, 10 (1986).
2. M. Shirai, T. Masuda, M. Tsunooka, and M. Tanaka, *Macromol. Chem. Rapid Commun.*, **5**, 689 (1984).
3. F. M. Houlihan, A. Shugard, R. Gooden, E. Reichmanis, *Macromolecules*, **21**, 2001 (1988).
4. W. Brunsvold, R. Kwong, W. Montgomery, W. Moreau, H. Sachdev, K. Welsh, *Proc. SPIE*, **1262**, 162 (1990).
5. K. H. Chae, I. K. Park, and M. H. Choi, *Bull. Korean Chem. Soc.*, **15**, 614 (1993).
6. C. A. Renner, *U. S. Patent* 4,371,605, DuPont (1980).
7. K.-J. Przybilla, R. Dammel, G. Pawlowski, H. Roschert, and W. Spiess, *Polym. Eng. & Sci.*, **32**, 1516 (1992).