NEW NEGATIVE-TYPE PHOTOSENSITIVE POLY(PHENYLENE ETHER) : Poly(2-hydroxy-6-methylphenol-co-2,6-dimethylphenol), a Cross-Linker, and a Photoacid Generator

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ABSTRACT

INTRODUCTION

Thermal stable and photosensitive polymers, especially photosensitive polyimides (PSPIs) are used as protection and insulation layers of very large scale integration circuit (VLSI), multi-chips modules for computers.[1)] We have been interested in developing thermal stable imaging materials that can be used as a substitute of PSPI.

In a previous paper[2)], we reported the new positive working alkaline developable thermally stable and photosensitive polymer based on poly(2-hydroxy-6-methylphenol-co-2,6-dimethylphenol) (PHP-MP) and 2,3,4-tris[2-diazo-1(2H)-naphthalenone-4-sulfonyloxy]benzophenone as a photoreactive compound. However, its sensitivity and contrast were 75 mJ/cm^2 and 1.5 with 365 nm light. Furthermore, a 10 % weight loss of polymer was at 360 °C. These properties are not enough to constitute a thermally stable and photosensitive polymer.

To improve the sensitivity, contrast, and thermal stability, we introduced a chemically amplified system, specially an acid-catalyzed cross-linking one into PHP-MP

In this paper, we report a three-component negative type alkaline developable thermally stable and photosensitive polymer based on PHP-MP, 4,4 1 -methylenebis[2,6-bis(hydroxymethyl)]phenol (MBHP) as a cross-linker, and a photoacid generator diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS).

Experimental

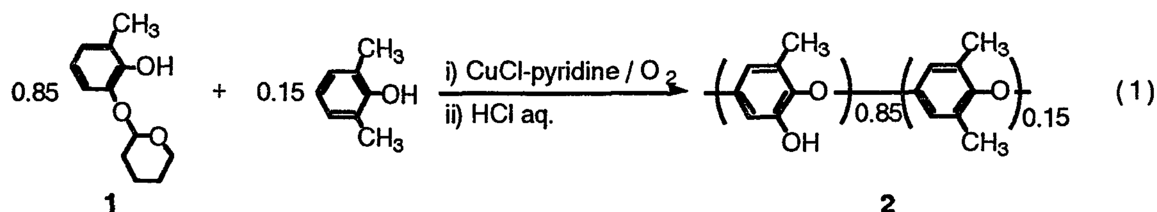
Materials. 4,4'-Methylenebis[2,6-bis(hydroxymethyl)]phenol (MBHP)[3)] and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS)[4)] were prepared according to literature procedures.

Synthesis of poly(2-hydroxy-6-methylphenol-*co*-2,6-dimethylphenol) (2). Polymer **2** was prepared by the oxidative coupling polymerization of 2-hydroxy-6-methylphenol **1** with 2,6-dimethylphenol according to a reported procedure[2)].

Results and Discussion

Synthesis of poly(2-hydroxy-6-methylphenol-*co*-2,6-dimethylphenol) (2). The synthesis of polymer **2** was carried out by the oxidative coupling polymerization of 2-(tetrahydropyran-2-yl)oxy-6-methylphenol **1** with 2,6-dimethylphenol in the molar ratio of 0.85 : 0.15 in the presence of copper(I) chloride and pyridine in toluene, then followed by acid cleavage of the protecting group (eq. 1). The structure of polymer **2** was confirmed as the desired poly(hydroxyphenylene ether) by IR and ^{1}H- and ^{13}C-NMR spectroscopies.

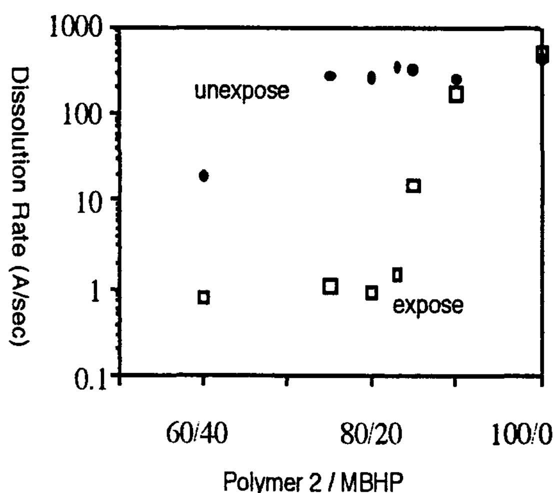
The molecular weight of the polymer was estimated(relative to a polystyrene standard) by gel permeation chromatography (GPC) in THF. The chromatogram of polymer **2** should unimodal distribution and indicated that the Mn and Mw were 9100 and 22000, respectively.



Lithographic Evaluation. As polymer **2** has no absorption above 300 nm, DIAS having a strong absorption in the range of 300-420 nm was selected. On the other hand, MBHP as a acid-catalyzed cross-linker was used on the bases of its availability and high reactivity.

The effect of the MBHP loading on the dissolution rate in a 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) solution after exposure of 30 mJ/cm^2 and PEB at 125 °C for 3 min was studied, and the results are shown in Figure 1. It was found that a 18 wt% MBHP loading was necessary to achieve adequate dissolution contrast.

To determine post exposure bake (PEB) temperature, we measured the dissolution rates of both exposed and the unexposed areas at various PEB temperature. The results of the resist formulated by mixing polymer **2** (72 %), MBHP (18 %), and DIAS (10 %) in cycrohexanone are shown in Figure 2, where the film was exposed 30 mJ/cm^2 to i-line, postbaked at elevated temperature from 80 to 150 °C for 3 min, and developed with the 2.38 wt% aqueous. TMAH developer. The dissolution rate of the exposed region was decreased by an increase of PEB temperature. On the other hand, the solubility of unexposed area was almost unchanged below 130 °C, but decreased at 140 °C. This temperature is higher than the melting point of MBHP and the cross-linking would take place thermally by the melt MBHP. The difference of the dissolution rates between exposed and unexposed parts reached about 300 times at 125 °C for 3 min. Thus the suitable PEB temperature was 125 °C.



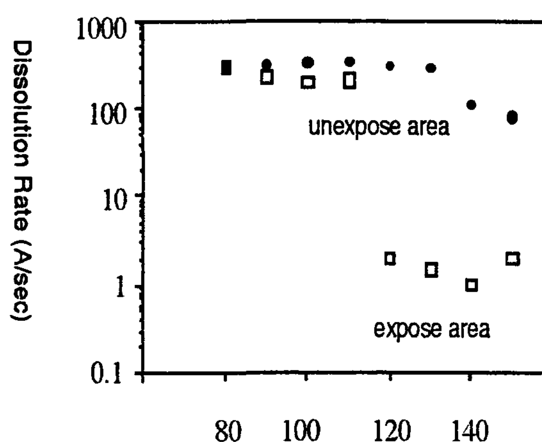
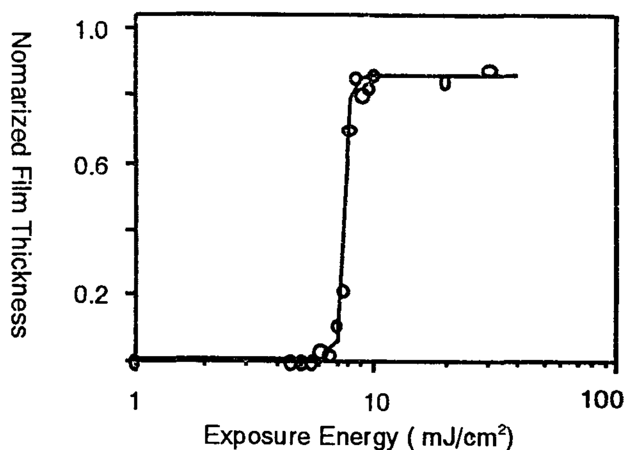


Figure 1. Relationship between MBHP content and dissolution rate

Figure 2. Effect of PEB temperature on the dissolution rate of polymer **2** film containing MBHP and DIAS

After these preliminary optimization, we formulated a photosensitive polymer system consisting of polymer 2 (72 %), MBHP (18 %) and DIAS (10 %) in cyclohexanone. The sensitivity curve for a 1.6 mm thick polymer 2 film, shown in Figure 3, indicates that the sensitivity ($D_{0.5}$) and contrast ($r_{0.5}$) were 7.9 mJ/cm^2 and 9.3, respectively. Figure 4 presents a scanning electron micrograph of the contact-printed image that was obtained using the resist system , exposured to 11 mJ/cm^2, post-exposure baked at 125 °C for 3 min, and developed with the 2.38 % aqueous TMAH solution at room temperature. The clear negative pattern with 2 mm resolution was obtained.



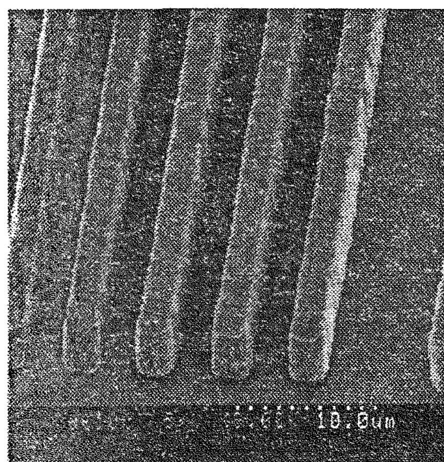


Figure 3. Exposure characteristics curve for the system of polymer **2**, MBHP and DIAS

Figure 4. SEM of the pattern from the system containing polymer **2**

Thermal Stability of polymer films. Figure 5 shows TGA curve of film after postbaking at 125 °C for 3 min and then developing at room temperature and curing 300 °C for 1 hour. No weight loss was observed below 350 °C, and the 10 % weight loss temperature was 420 °C. This temperature is higher than that of polymer **2** because of the formation of a cross-linked polymer. These results indicated that DIAS can be removed by high temperature treatment and the thermal properties of the resulting polymer have not dameged such as degradation of DIAS. Furthermore, this negative image in the polymer **2** film treated at the 300 °C for 1 h had not any deformation (Figure 6).

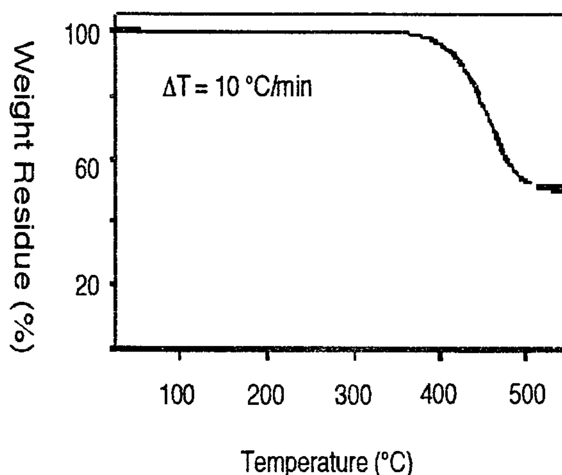


Figure 5. TG curve of the polymer **2** system after thermal treatment

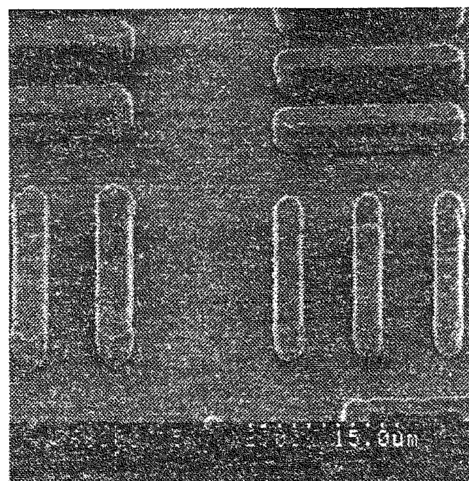


Figure 6. SEM of the thermally treated pattern

Conclusion

Polymer **2** was prepared by oxidative coupling polymerization of **1** with 2,6-dimethylphenol. The photochemical reaction of DIAS in the polymer **2** film occurred smoothly because of its excellent transparency in the UV region above 300 nm. This system was formulated by mixing the polymer **2** (72 %), MBHP (18 %), and DIAS (10 %) in cycrohexanone and was found to be an alkaline-developable negative-type photosensitive polymer. The heat-treated negative image clearly reveals the high thermal stability.

References

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