

A new photoresist based on hyperbranched poly(arylene ether phosphine oxide)

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Summary

Hydroxy-terminated hyperbranched poly(arylene ether phosphine oxide) (**P2**) was synthesized *via* nucleophilic aromatic substitution reaction of AB₂ monomer, bis(4-hydroxyphenyl)-4'-fluorophenylphosphine oxide with K₂CO₃ as a base in NMP. The obtained polymer was dissolved well in NMP and DMSO, and casting of the solution gave a transparent film. The study on dissolution behavior of the film containing 10 wt% of diphenyliodonium-9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator and 25 wt% of 4,4'-methylenebis-[2,6-bis(hydroxymethylphenyl) phenol] (MBHP) as a cross linker revealed that 0.5 wt% aqueous tetramethylammonium hydroxide (TMAH) solution was a suitable developer for this negative-type photoresist system. The photoresist system containing 10 wt% of DIAS and 25 wt% of MBHP showed the sensitivity of 9 mJ/cm² and the contrast of 1.6 when it was exposed to 365 nm light and postbaked at 120°C, followed by developing with 0.5 wt% aqueous TMAH solution at room temperature. The heat-treated (300°C, 30 min) negative image did not show any distortion.

Introduction

Recently, three-dimensional polymers, such as dendrimeric and hyperbranched macromolecules, have received considerable attention because of the pre-determined structure and unique properties at the nano-scale region [1-5]. There are a number of similarities and differences between these two families of three-dimensional macromolecules. The similarities arise from AB_x type compounds being used to prepare both macromolecules. However, the synthetic approaches used for both families of macromolecules are very different and this leads to great difference in structure. While the perfectly branched and monodisperse dendrimers are prepared by either a step-wise divergent or convergent approach, hyperbranched macromolecules are prepared in a one-step polymerization process that gives irregular and polydisperse

structures with random branching. Advantage of this one-step approach is that hyperbranched macromolecules can be obtained much more easily than comparable dendrimeric macromolecules, which is desirable for many practical applications including coating, membrane, and nanocomposite material[6-9].

Recently, we have been interested in new photoresist material based on some dendrimeric and hyperbranched polymers[10-12]. Due to their highly branched globular structures, the large number of reactive end groups locate at the periphery of macromolecules, where they can react with other functional groups easily and efficiently. The above characteristics of dendrimer and hyperbranched polymers may provide an improved resist performance when they are utilized as a matrix material of resists.

In this article, we report the development of a new negative-working, alkaline-developable photoresist consisting of the hydroxy-terminated hyperbranched poly(arylene ether phosphine oxide) (**P2**), a photoacid generator (DIAS) and a cross linker (MBHP). The presence of phosphorous oxide groups in polymers is expected to enhance atomic oxygen plasma resistance through the formation of an inorganic phosphate-type species during dry etching that provides a simplified and improved pattern fabrication process[13-15].

Experimental

Measurements

The UV spectra were obtained on a Shimadzu UV-2200 spectrometer. Thermogravimetric analyses (TGA) were performed on a Seiko SSC/5200 (TG/DTA 220) thermal analyzer at a heating rate of 10°C/min. The differential scanning calorimetry (DSC) was performed on a Seiko SSC/5200 (DSC 220) instrument at a heating rate of 20°C/min under nitrogen atmosphere. The film thickness was measured by a Dektak 3030 system (Veeco Instrument Inc.). The scanning electron micrographs were obtained with a JEOL 5300 scanning electron microscope.

Materials

Bis(4-methoxyphenyl)-4'-fluorophenylphosphine oxide (**1**) was prepared as previously reported.[16,17]. Methylene chloride, dimethyl sulfoxide, and NMP were distilled over CaH₂. Imidazole, t-butyltrimethylsilylchloride, potassium carbonate, cesium carbonate, diphenyl sulfone, cesium fluoride, magnesium hydroxide, acetic acid, hydrobromic acid and BBr₃ were purchased from Aldrich and Tokyo Kasei Co. and used without further purification.

Synthesis of Bis(4-hydroxyphenyl)-4'-fluorophenylphosphine oxide (2).

Compound **1** (12.338 g), 45 mL of glacial acetic acid and 35 mL of hydrobromic acid (HBr; 48%; Aldrich) were placed in a 250-mL, three-neck flask, and the reaction mixture was heated at 125°C for 21 hrs under a nitrogen purge until the solution changed to a dark brown color. After cooling, the crude solution was poured into 500 mL of distilled water, and the precipitated product was collected with a glass filter. After column chromatography (MC:MeOH=10:1), white solid was obtained. Yield = 90%. M.P. = 230°C. FT-IR(KBr,cm⁻¹) 3360, 1601, 1504, 1437, 1161. ¹H-NMR

(DMSO- d_6 , ppm) δ = 10.08 (s, 2H, -OH), 7.64-7.56 (m, 2H), 7.40-7.29 (m, 6H), 6.90-6.86 (dd, 4H). ^{13}C -NMR(DMSO- d_6 , ppm) δ = 165.4, 162.9, 160.8, 134.4, 133.5, 131.0, 129.9, 122.5, 121.4, 116.0, 115.7.

Polymerization

AB₂ monomer **2** was polymerized in NMP with K₂CO₃ or Cs₂CO₃/Mg(OH)₂ as a base between 170°C and 190°C. A representative procedure is as follows. A 25 mL three-neck flask fitted with a dean stark trap was charged with 0.50 g of bis(4-fluorophenyl)-4'-hydroxyphenylphosphine oxide and 0.44 g of K₂CO₃. The concentration was controlled to 25 wt% in NMP and small amount of toluene was added to effect the azeotropic removal of water. The mixture was stirred and heated to 140°C, at which toluene was collected and removed from the system. The temperature was maintained for 4 hrs, and additional toluene was periodically added and subsequently collected and drained from the trap. The mixture was then heated to 170°C for 4 hrs. After that, the mixture was allowed to cool and then poured into 200 mL water. The precipitated **P2** was washed with MeOH and dried overnight at 120°C *in vacuo*. FT-IR(KBr,cm⁻¹) 3440, 1581 1493,1284,1119. ^1H -NMR (DMSO- d_6 , ppm) δ = 10.08 (s, 1H, -OH), 7.64-7.57 (m, 4H), 7.41-7.32 (m, 2H), 7.21-7.18 (m, 4H), 6.90-6.85 (m, 2H).

Dissolution Rate Measurements

To the 25 wt% NMP solution of hyperbranched polymer **P2** were added MBHP and DIAS (25 wt% and 10 wt% of the total solid, respectively). Films obtained by spin-coating of the solution on Si wafer were prebaked at 120°C for 10 min and then exposed through a filtered super-high pressure mercury lamp SH-200 (Toshiba Lighting and Technology Corporation). Imagewise exposure was carried out in a contact mode. Exposed films were subjected to development with 0.5 wt% aqueous TMAH solution at room temperature after postbaking. The dissolution rate was determined by measuring the change of film thickness per development time.

Photosensitivity

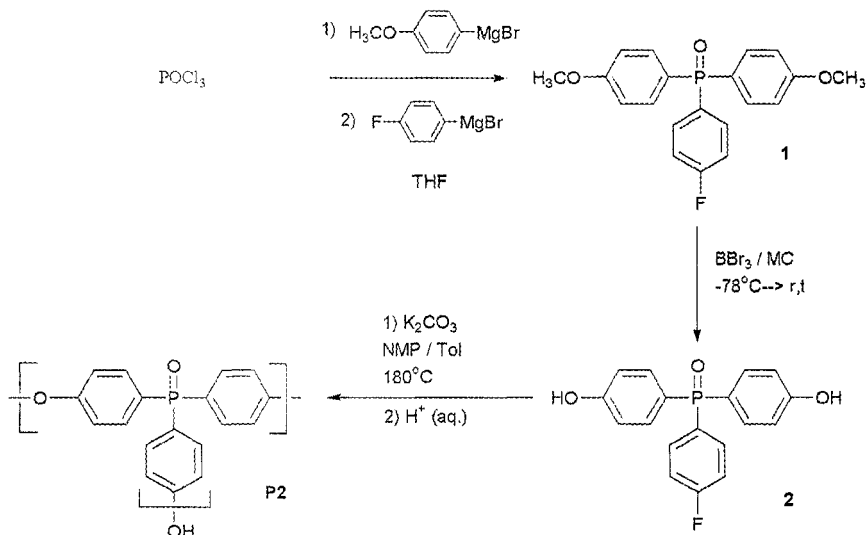
One-micrometer films on silicon wafers were exposed to 365 nm UV (super-high mercury lamp) and then they were baked at 120°C for 7 min. The film were developed in a 0.5% aqueous TMAH solution at room temperature, and rinsed with water. The characteristic curve was obtained by plotting normalized thickness against exposure energy.

Results and Discussion

Synthesis of hydroxy-terminated hyperbranched poly(arylene ether phosphine oxide) (P2)

AB₂ type monomer **2** containing two hydroxy groups and one fluorine group activated by electron withdrawing phosphine oxide group was prepared by sequential addition of methoxyphenyl magnesium bromide and 4-fluorophenyl magnesium bromide to phosphorous oxychloride as previously reported[16]. Demethylation of resulting

bis(4-methoxyphenyl)-4'-fluorophenylphosphine oxide **1** with BBr_3 or aq. HBr yielded the desired monomer **2**, quantitatively [16,17].



Scheme 1. Synthesis of AB_2 Monomers **2** and Polymerization to Hyperbranched Polymers **P2**

The synthesis of **P2** was carried out by the nucleophilic aromatic substitution reaction of this AB_2 -type monomer **2** as shown in Scheme 1. For the resist application, the polymer should have good film forming ability, but generally hyperbranched polymers have rather low solution viscosity and do not form a good quality film. In order to control the quality of spin-coated polymer film, polymerization of the AB_2 monomers were carried out at various condition (temperature, solvent, and inorganic bases). The optimal result in viscosity and yield of the polymer was obtained at 180°C in NMP. The polycondensation proceeded in a slightly heterogeneous solution mixture, but after acidic workup, the polymer was completely soluble in NMP and DMSO with an inherent viscosity of 0.18 dL/g.

The structure of the **P2** was confirmed with FT-IR and $^1\text{H-NMR}$. The FT-IR spectrum showed the characteristic absorptions of aryl ether linkage at 1242 cm^{-1} and the absorption of the hydroxy end groups at 3440 cm^{-1} . The $^1\text{H-NMR}$ spectrum showed all the peaks corresponding to the structure of the repeating unit, but the calculation of degree of branching was impossible because of overlapping of the resonance peaks.

P2 was soluble in NMP and DMSO, but insoluble or partially soluble in other organic solvents. The polymer was also soluble in aq. NaOH or tetramethylammonium hydroxide (TMAH), presumably due to the large number of hydroxy end-group at the periphery of the globular structure of hyperbranched polymer. Transparent film was cast from the solution of the **P2** in NMP but hexamethyldisilazane (HMDS) treatment of a silicon wafer was required for the good film casting.

The thermal behavior of **P2** was studied by thermogravimetry analysis (TGA). 10% Weight loss of **P2** occurred at 450°C in nitrogen. Differential scanning calorimetry did not show any clear endotherms until 350°C , indicating amorphous nature of **P2**.

Lithographic Evaluation

The transmission UV-visible spectrum of a 1 μm thick **P2** film is shown in Figure 1. The **P2** film shows strong absorption with a cutoff near 300 nm. The transmittance at 365 nm is over 96%.

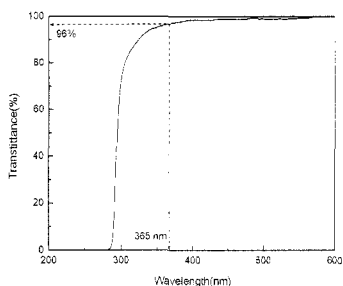


Figure 1. UV-visible spectrum of P2.

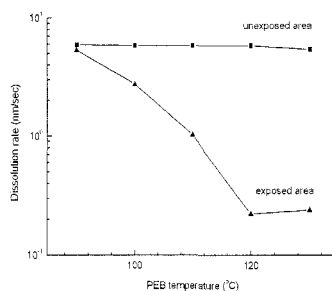


Figure 2. The effects of postexposure bake temperature on the dissolution rate (PEB time; 3 min).

The three-component negative-type photoresist was formulated from **P2**, 4,4'-methylenebis[2,6-bis(hydroxymethyl)phenol] (MBHP) as a cross-linker, and a diphenyliodonium-9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator. The dissolution behavior of the exposed and unexposed areas, and the effect of the post-exposure bake (PEB) temperature and time was studied. The dissolution rate was estimated by measuring the residual film thickness after the development. The results of dissolution rate study of the resist consisting of **P2** (65 wt %), MBHP (25 wt %), and DIAS (10 wt %) in NMP are shown in Figure 2 and Figure 3, where the film was exposed to 365 nm UV light ($15\text{mJ}/\text{cm}^2$), postbaked and developed with the 0.5 % aqueous TMAH solution. The dissolution rate of the exposed part decreased with increasing PEB temperature. On the other hand, the solubility of unexposed area was almost unchanged. The difference of the dissolution rates between the exposed and unexposed parts reached about 23 times after PEB at 120°C for 3 min. The dissolution rate became constant after 3 min PEB at 120°C as shown in Figure 3. These results suggest that PEB treatment promotes the cross-linking reaction through electrophilic aromatic substitution.

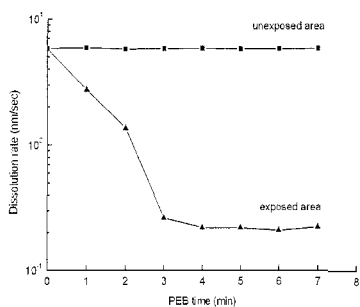


Figure 3. The effects of postexposure bake time on the dissolution rate (PEB temperature; 120°C).

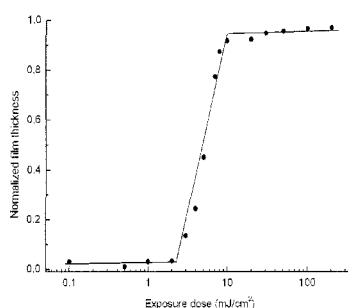


Figure 4. Exposure characteristic curve of resist consisting of **P2**, MBHP, and DIAS.

After the preliminary optimization studies involving PEB temperature and PEB time, a resist system consisting of **P2** (65 wt %), MBHP(25 wt %), and DIAS(10 wt %) in NMP was formulated. The film spin-cast on silicon wafer after HMDS treatment was prebaked at 120°C for 10 min (thickness of 1 μm), exposed to 365 nm UV radiation, postbaked at 120°C for 7 min, and developed in a negative-mode with the 0.5% aqueous TMAH solution at room temperature. The sensitivity curve (Figure 4) revealed that the sensitivity ($D^{0.5}$) and contrast ($\gamma^{0.5}$) were 9 mJ/cm^2 and 1.6, respectively.

A clear negative pattern with 0.55 μm resolution was obtained using the resist described above after exposure to 15 mJ/cm^2 , PEB at 120°C for 7 min, and developing with the 0.5% aqueous TMAH solution. A scanning electron micrograph of the negative images heated at 300°C for 30 min does not show any distortion in Figure 5, revealing the high thermal stability of the resist.

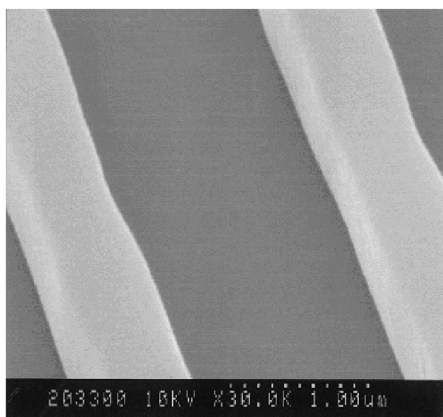


Figure 5. Scanning electron micrograph of the negative image printed in the **P2** system after heating at 300°C for 30 min.

Conclusions

The hyperbranched poly(arylene ether phosphine oxide) **P2** which has an excellent transparency in UV-region was prepared from AB_2 -type monomer **2** via nucleophilic aromatic substitution reaction polymerization. The mixture consisting of **P2** (65 wt %), MBHP(25 wt %), and DIAS(10 wt %) was found to be an alkaline-developable negative-type photosensitive resist with the sensitivity of 9 mJ/cm^2 .

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