New Negative-Type Photosensitive Polyimide Based on Hyperbranched Poly(ether imide), a Cross-Linker, and a Photoacid Generator

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A new negative working photosensitive polyimide, based on hyperbranched poly(ether imide) (**1**), 4,4'-methylenebis[2,6-bis(hydroxymethyl)]phenol (**2**) as a cross-linker, and a photoacid generator diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (**3**) has been developed. **1** was prepared by polycondensation of *N*-[3,5-di-(*tert*-butyldimethylsilyloxy)phenyl]-4-fluorophthalimide (**4**), followed by deprotection of *tert*-butyldimethylsilyl group with KF-HBr. The photosensitive polyimide containing **1** (70 wt%), **2** (20 wt%) and **3** (10 wt%) gave a clear negative pattern when it was exposed to 365 nm light and postbaked at 120 °C, followed by developing with a 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) solution at room temperature.

Polyimides have excellent electrical property and high thermal stability for application in microelectronics industry.

Photosensitive polyimides (PSPIs) are widely applied as protection and insulation layers in manufacturing semiconductor because the number of processing steps is simplified by avoiding the use of usual photoresists. Although various negative and positive type PSPIs have been reported up to now,[1,2] most of these resist systems require thermal treatment in high temperature for the imidization after development, which is not suitable for semiconductor manufacturing. For example most of the negative-type PSPIs are prepared from poly(amic acid)s containing photo-polymerization sites such as acryloyl groups on the polymer backbone.[3] The positive-type PSPIs consist of poly(amic acid)s and dissolution inhibitors such as *o*-diazonaphthoquinone, 1,4-dihydropyridine derivatives,[4,5] and *o*-nitrobenzyl esters of poly(amic acid).[6] Furthermore, both negative and positive type alkaline developable PSPIs based on poly(hydroxyimide)s as a matrix have been reported.[7,8] Most of the standard resist materials used in semiconductor manufacturing are an alkaline developable positive type resist based on novolac resin with diazonaphthoquinone. Thus, aqueous alkaline developable PSPIs are preferable to PSPIs developed with organic solvents.

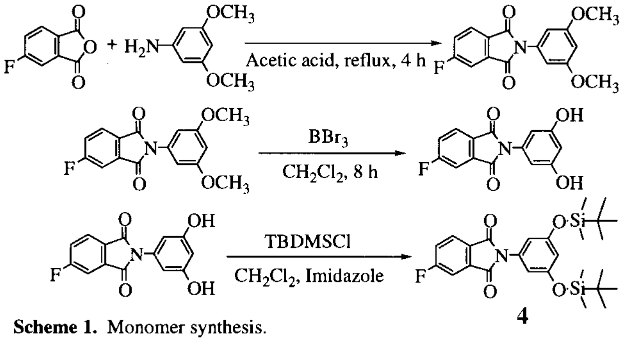
In general, these polyimide matrixes have a poor solubility for organic solvents and a problem to introduce alkaline developable functional groups.

Recently, hyperbranched polymers have been receiving a great attention for their unique properties such as intrinsic globular structure, low viscosity, high solubility and large number of terminal functional groups. There have been many reports on the synthesis and characterization of hyperbranched polymer, and various applications such as blend components, nanoforms, nonlinear optics and catalysts.[9,10] However, little work has been done for testing potential application to photosensitive materials because of poor mechanical properties of those films.

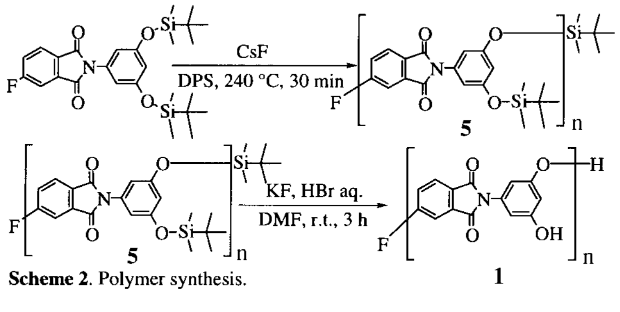
To remedy these problems, an acid-catalyzed cross-linking system into hyperbranched polymers is suitable. And, hyperbranched poly(ether imide)s having imide backbones and many phenolic hydroxy groups on terminal units would be a good candidate as a matrix polymer for developing the alkaline developable photosensitive materials

This paper describes the synthesis of a negative-type alkaline developable PSPI system based on hyperbranched poly(ether imide) **(1)**, 4,4'-methylenebis[2,6-bis(hydroxymethyl)] phenol (**2**) as a cross-linker and a photoacid generator diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (**3**).

Recently, Moore et al. reported the synthesis of hyperbranched polymer **1** from *N*-[3,5-di(*tert*-butyldimethylsilyloxy)phenyl]-4-fluorophthalimide **(4)** as an AB_2 monomer.[11] Thus, polymer **1** was selected as the matrix polymer for the formation of a new photosensitive system. Monomer **4** was prepared as shown in Scheme 1, which is different from the reported method.[11] Polymerization of monomer **4** was carried out in diphenyl sulfone (DPS) in the presence of cesium fluoride at 240 °C for 30 min, giving TBDMS-protected polymer **5** (TBDMS = *tert*-butyldimethylsilyl) and deprotection of TBDMS groups was achieved with KF–HBr (Scheme 2). The polymer was identified as the corresponding **1** by IR, ^{1}H and ^{13}C NMR spectroscopies.[11] The degree of branching determined by ^{1}H NMR spectroscopy was 50%. The molecular weight of the polymer



Scheme 1. Monomer synthesis.



Scheme 2. Polymer synthesis.

was determined by GPC. The chromatogram was a unimodal distribution, and indicated the M_n and M_w values were 27000 and 60000, respectively, using polystyrene standard, and the ratio of M_w/M_n was 2.2.

The thermal stability of **1** was examined by thermogravimetry (TG) and differential scanning calorimetry (DSC). The polymer showed a 10% weight loss at 500 °C in nitrogen and the glass transition temperature was observed at 250 °C (Figure 1). The transmission of UV–vis spectrum of **1** in DMF solution was measured. It was found that an i-line (365 nm) irradiation was possible for this polymer because the transmittance of **1** at 365 nm was more than 90%.

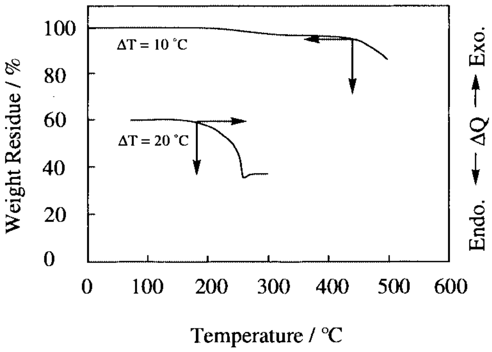


Figure 1. TGA and DSC curves of Polymer **1** in nitrogen.

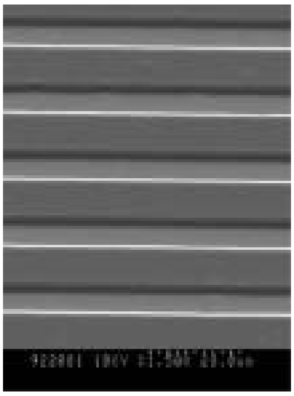
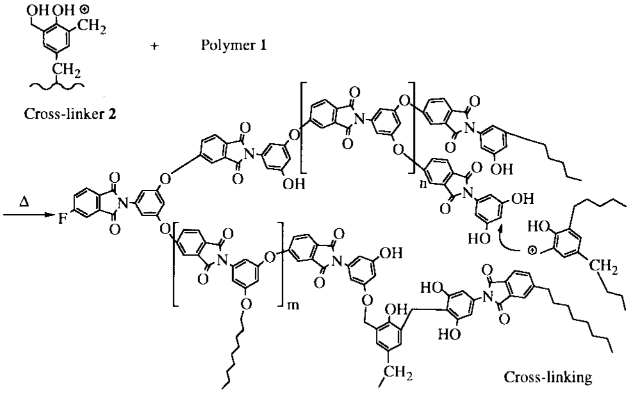


Figure 2. Scanning electron micrograph of the negative image printed in the polymer **1** system.

We formulated a photosensitive polyimide system consisting of **1** (70 wt%), **2** (20 wt%), and **3** (10 wt%) in 2-methoxyethanol. In Figure 2 is presented a scanning electron micrograph of the contact-printed negative image that was postbaked at 120 ˚C for 5 min after exposure to 200 mJ·cm^{-2}, and developed with a 2.38 wt% aqueous tetramethylammonium hydroxide solution. The resist is capable of resolving 4.5 µm features when 1.4 µm thick film is used. A photogenerated acid catalyzes the formation of benzylic carbocation speices, which undergo electrophilic aromatic substitution to produce a *C*- and *O*-alkylated polymers. This reaction converts the soluble polymer **1** to insoluble cross-linked polymer (Scheme 3).[8] To achieve an excellent resolution, a detailed optimization study involving the loading **2** and **3**, and postbaked temperatures is in progress.



Scheme 3. Mechanism of cross-linking.

References and Notes

1 R. Rubner, H. Ahne, and E. Kunh, *Photogr. Sci. Eng.*, **23** (5), 303 (1979).

2 T. Omote, in “Polyimide, ” ed. by M. K. Gosh and K. L. Mittal, Marcel Dekker, Inc., New York (1996) p 121.

3 Y. Yoda, T. Morikawa, T. Ando, and A. Fukami, *J. Macromol. Sci. Chem.* **A-21**, 1641 (1984).

4 S. Hayase, K. Takano, Y. Mikogami, and Y. Nakano, *J. Electrochem. Soc.*, **138**, 3625 (1991).

5 T. Omote and T. Yamaoka, *Polym. Eng. Sci.*, **32** 1634 (1992).

6 S. Kubota, T. Morikawa, T. Ando and J. Fukami, *J. Macromol. Sci. Chem.*, **A-24**, 1407 (1987).

7 T. Nakayama, A. Mochizuki, and M. Ueda, *Reac. Polym.* **30**, 109 (1996).

8 M. Ueda and T. Nakayama, *Macromolecules*, **29**, 6427 (1996).

9 Y. H. Kim, *J. Polym. Sci., Part A: Polym. Chem.* **36**, 1685 (1998).

10 B. Voit, *J. Polym. Sci., Part A: Polym. Chem.* **38**, 2505 (2000).

11 D. S. Thompson, J. L. Markoski, and J. S. Moore, *Macromolecule*, **32**, 4764 (1999).