Preparation of Fully Imidized Hyperbranched Photosensitive Polyimide with Excellent Organosolubility and Thermal Property Based on 4,4'-(Hexafluoroisopropylidene) Diphthalic Anhydride (A_2) and 1,3,5-Tris(4-aminophenoxy)benzene (B_3)

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Summary

A negative-tone hyperbranched photosensitive polyimide (HB-PSPI) based on a new triamine, 1,3,5-tris(4-aminophenoxy)benzene (TAPOB), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) was synthesized. The photosensitive cinnamate groups were incorporated at the periphery of the polymer by the reaction of cinnamoyl chloride with the terminal phenol groups of the fully imidized hyperbranched polyimide, which was obtained via the end group modification of the anhydride-terminated hyperbranched poly(amic acid) precursor. The polymer showed good thermal property with 10 wt % loss temperature at 517 °C, and exhibited excellent organosolubility even in acetone and 1,1,2-trichloroethane. Photolithographic property of the polymer was examined by UV exposure. SEM analysis revealed that highly resolved patterns with a line width of 10 µm were obtained; and well-defined line as thin as 3µm in width could be patterned, though the line edges were jagged and rounded due to the broad molecular weight distribution.

Introduction

Polyimides have been widely used as high temperature insulators and dielectrics, coatings, adhesives and matrices in a variety of advanced technologies related to microelectronics, where miniaturization and large-scale integration are important technical issues [1,2]. The application of photosensitive polyimides (PSPIs), which can be directly patterned by exposure to light, simplifies greatly the complex multistep imaging schemes involved in the conventional nonphotosensitive polyimide photolithography processes [1]. Up to now, many types of PSPIs and their precursors have been prepared and put into industrial use [1,2]. Being insoluble in most common solvents, polyimides are usually processed in the form of their procursor poly(amic acid)s, which are then thermally converted to the imido structure. However, this method is sometimes difficult to apply in practical processs because of the high

temperature required for imidization, and the substantial shrinkage of the layer resulting from the removal of small molecules during thermal cyclization [1]. Therefore, fully imidized PSPIs with good solubility in common organic solvents are desired to apply as photoresist materials.

Hyperbranched polymers have received considerable attention in the past decade due to their unique physical and chemical properties compared with linear polymers, such as low solution viscosity, high organic solubility and a large number of terminal reactive groups [3-7]. Functionalization of the polymers can be easily fulfilled by the incorporation of functional groups at the periphery of the global molecules. These types of functional materials are thought to have high functionality because of the decreased chain entanglement and the peripheral location of the functional groups [5,6]. Among them, photoresist materials seem to be a promising family. Since the highest resolution is in the order of the size of the individual pixels that compose the image, photoresist materials based on dendritic macromolecules might potentially offer high resolution and photosensitivity due to their compact molecular size and high functionality of the peripheral photosensitive groups [8-10]. Some attempts on hyperbranched polymer and dendrimer-based resist materials have already been reported recently [8-12].

Hyperbranched polyimides based on a novel triamine (B_3), 1,3,5-tris(4-aminophenoxy)benzene (TAPOB), and commercially available dianhydrides (A_2) have been prepared recently in our lab, and showed rather good solubility even in low boiling point solvents, such as THF, chloroform, and acetone [13]. Different monomer addition manners and molar ratios of monomers resulted in hyperbranched polyimides with amino- or anhydride-terminated groups. In this paper, we report our initial attempt on the synthesis of a negative-tone hyperbranched photosensitive polyimide (HB-PSPI) based on TAPOB and 4,4_-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). The photosensitive cinnamate groups were incorporated at the periphery of the dendritic macromolecules by the reaction of cinnamoyl chloride in the catalysis of triethylamine in NMP with the terminal phenol groups of the fully imidized hyperbranched polyimide, which was obtained via the modification of the end groups of the anhydride-terminated hyperbranched poly(amic acid) precursor with 4-aminophenol during the course of polymerizaiton.

Experimental

Chemicals

N-methyl-2-pyrrolidone (NMP) was distilled from calcium hydride under reduced pressure. 4,4_-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) was obtained commercially, and purified by recrystallization from acetic anhydride before use. 1,3,5-Tris(4-aminophenoxy)benzene (TAPOB) was synthesized in our lab [13]. Other solvents and reagents were used as received.

Measurements

Infrared spectra (IR), differential scanning calorimetry (DSC, at a heating rate of 10 ˚C/min in nitrogen) and thermogravimetric analysis (TGA, at a heating rate of 20 ˚C/min in nitrogen) were recorded on FTIR Paragon 1000, DSC Pyris 1 and TGA-7 of

Perkin-Elmer, respectively. ^{1}H NMR spectra were performed on a Mercury 400MHz spectrometer using DMSO-d_6 as the solvent. Elemental analysis was conducted on an Elementar Varioel apparatus. Molecular weights were determined by gel permeation chromatography (GPC) using polystyrene as a standard on a Perkin-Elmer Series 200 apparatus equipped with Polymer-Lab Mixed 10 μ column. The eluant was tetrahydrofuran (THF) with a flow rate of 1.0 ml/min at 25 °C. The polyimide patterning profiles were obtained with a HITACHI S-2150 scanning electron microscope (SEM). The sample was homogeneously coated with a very thin layer of gold using a SEM coating unit prior to analysis.

Synthesis of Hyperbranched Polyimide with Terminal Phenol Groups (HB-PI-(OH)$_n$) (Scheme 1)

5 mmol of dianhydride 6FDA was dissolved in 30 ml of NMP in a 150 ml thoroughly dried three-neck flask under nitrogen flow. To the mixture was dropwise added 2.5 mmol of TAPOB in 30 ml of NMP through a syringe over 1 h under magnetic stirring at 40 °C. An excessive amount of 4-aminophenol (3 mmol) was added to the mixture 4 h later, and the reaction was further conducted for 5 h at 40 °C. Then a mixture of 5 g of triethylamine and 15 g of acetic anhydride was added, and the reaction mixture was stirred at 40 °C for 12 h. After cooling to room temperature, the mixture was precipitated from 700 ml methanol. The polymer was collected by filtration and dried in vacuum at 80 °C for 24 h.

Synthesis of Hyperbranched Photosensitive Polyimide (HB-PSPI) (Scheme 2)

5 mmol cinnamic acid was added to 15 ml thionyl chloride in a 100 ml three-neck round-bottom flask equipped with a reflux condenser, a nitrogen inlet, and a magnetic stirrer. The mixture was heated at reflux for 5 h. The excessive thionyl chloride was removed under reduced pressure. The yellow cinnamoyl chloride was dissolved in 10 ml NMP and added dropwise to a solution of 2 g HB-PI-(OH)$_n$ and 5 mmol triethylamine in 20 ml NMP over 1 h at 0 °C. After stirring for another 1 h at 0 °C, the mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was poured into 300 ml methanol and stirred mechanically for 5 h at room temperature. The precipitate was collected by filtration and dried in vacuum at 40 °C for 48 h.

Imaging of HB-PSPI

HB-PSPI was dissolved in 1,1,2-trichloroethane at a solid content of 10 wt %. Michler's ketone (5 wt % relative to HB-PSPI) was added as the photosensitizer. The solution was filtered through a 0.45 _m filter under pressure. The films were prepared by spin coating on clean glass substrates, and prebaked at 80 °C for 2 h. The thickness of the films was around 2 _m. The photoresist films were exposed in the contact mode with a mask for 4 min to a 250 W high pressure mercury lamp, which delivered a UV dose of 5.5 mJ/s with the strongest emission at 365 nm. The films were then developed in a mixture of 1,1,2-trichloroethane/2-propanol (9/1, v/v) for 60 seconds and rinsed with 2-propanol. After development, the patterns were dried at 150 °C for 5 h, and evaluated with scanning electron microscopy (SEM).

Results and Discussion

Polymerization

In previous work [13], we synthesized a series of hyperbranched polyimides based on a new triamine, 1,3,5-tris(4-aminophenoxy)benzene, and commercially available dianhydrides. The 6FDA-based hyperbranched polyimides showed very good solubility even in low boiling point solvent, such as THF, chloroform, 1,1,2-trichloroethane and acetone. Therefore, the 6FDA-based anhydride-terminated polyimide, which had better solubility than its amino-terminated counterpart, was selected as the macromolecule framework of photosensitive polyimide.

As shown in Scheme 1, a solution of triamine was added slowly enough to the reaction system containing 6FDA in a monomer molar ratio of 1/2 (molar ratio of amino and anhydride groups: 3/4) to afford an anhydride-terminated poly(amic acid). Subsequently, 4-aminophenol was added in one pot to convert the terminal anhydride groups to phenol groups. Then the polymer was imidized by chemical method at 40 °C to yield hyperbranched polyimide with terminal phenol groups (HB-PI-(OH)$_n$).
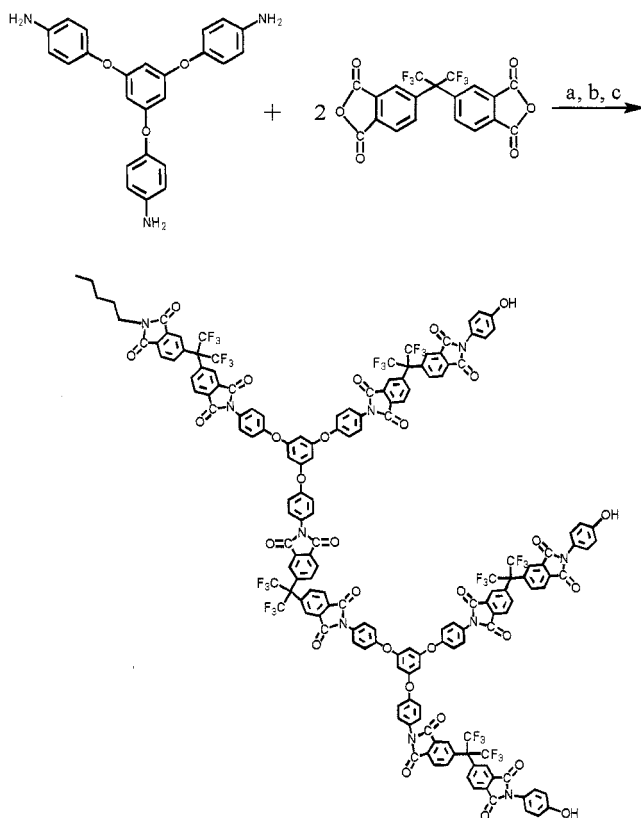
Scheme 1. Synthesis of Hyperbranched Polyimide with Terminal Phenol Groups (HB-PI-(OH)$_n$) *(a, a solution of TAPOB was dropwise added to the 6FDA solution over 1 h at 40 °C, additional 4 h at 40 °C; b, an excessive amount of 4-aminophenol was added, 5 h at 40 °C; c, chemical imidization, 5 g triethylamine and 15 acetic anhydride were added, 12 h at 40 °C)*
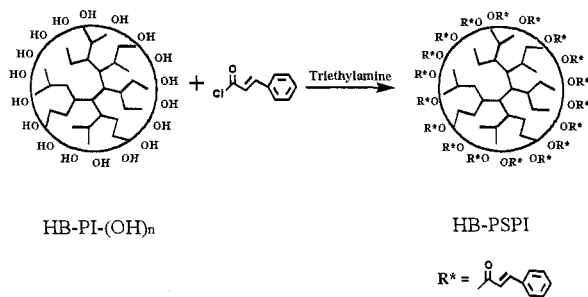
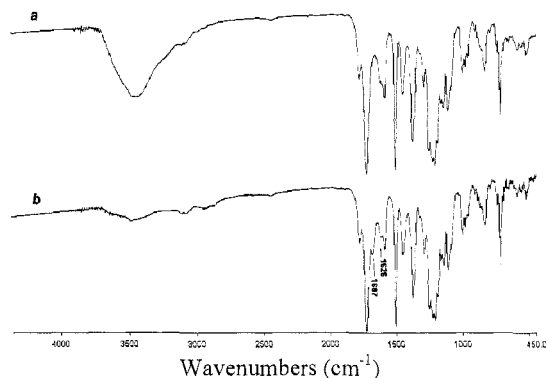**Scheme 2.** Synthesis of Hyperbranched Photosensitive Polyimide (HB-PSPI)

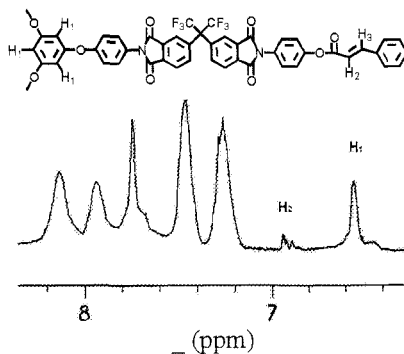**Figure 1.** IR Spectra of the Hyperbranched Polyimides (*a*, HB-PI-(OH)$_n$; *b*, HB-PSPI)

Figure 2. ^{1}H NMR Spectrum of Hyperbranched Photosensitive Polyimide (HB-PSPI)

The hyperbranched photosensitive polyimide (HB-PSPI) was prepared through the end group modification of the globe-structured HB-PI-(OH)$_n$, which was directly functionalized via the reaction of the terminal phenol groups with an excessive amount of cinnamoyl chloride in the catalysis of triethylamine in NMP (Scheme 2).

Figure 1 shows the FTIR spectra of the two polymers. The characteristic absorption bands of polyimides can be seen at 1785 cm^{-1}, 1727 cm^{-1} and 723 cm^{-1} from imide carbonyl groups, and at 1379 cm^{-1} from C-N groups for both polymers. No characteristic absorption band of poly(amic acid) (around 1680 cm^{-1}) was found for HB-PI-(OH)$_n$ (a), as indicates that full imidization of the polyimides was achieved.

The absorption bands at 1687 cm^{-1} and 1626 cm^{-1} for HB-PSPI can be attributed to the carbonyl groups and vinyl groups of the cinnamate segments, respectively (b). The terminal phenol groups of HB-PI-(OH)$_n$ generated a broad absorption band at 3100-3700 cm^{-1} (a), which almost disappeared in the spectra of HB-PSPI (b), as ascertains that the functionalization was achieved effectively.

Through ^{1}H NMR analysis (Figure 2), the functionalizing efficiency can be approximately estimated from the content of the photosensitive cinnamate groups. The broad peak around 6.53 ppm corresponds to the hydrogen H$_1$ of TAPOB residues [13], and the peaks around 6.96 ppm can be assigned to the vinyl proton H$_2$ [14]. In HB-PI-(OH)$_n$, the hydroxyl groups are equal to the TAPOB units in molar quantity at high molecular weight. Therefore, by comparing with the absorption intensities of H$_1$, which is equal to three times of the amount of original hydroxyl groups in molar quantity, and the H$_2$, which represents the cinnamate groups in HB-PSPI, the conversion efficiency of hydroxyl groups to cinnamate groups was evaluated to be 57%. The reason for low modification efficiency might be possibly due to the survival of thionyl chloride in cinnamoyl chloride solution, which reacted preferentially with the terminal phenol groups.

The molecular weights of the hyperbranched polyimides were determined by gel permeation chromatography (GPC) using THF as eluant. Table 1 shows the results of the GPC analysis relative to linear polystyrene standards. Both of the polymers exhibited a moderate molecular weight with a rather broad molecular weight distribution, to be 16.2 and 23.3 in polydispersity index for HB-PI-(OH)$_n$ and HB-PSPI, respectively. The reason has been well explained by Fang et al [15].

The molar ratio of TAPOB and 6FDA units (RM) in HB-PI-(OH)$_n$ was calculated to be 0.47 on the basis of the elemental analysis results (Table 2). Accordingly, we can deduce that the average molecular weight of HB-PI-(OH)$_n$ (M_c) is 11,218, which is quite in agreement with the experimental results by GPC (Table 1); and the average number of hydroxyl groups per HB-PI-(OH)$_n$ molecule (n) is 10. However, we cannot evaluate the composition of the monomer units in HB-PSPI, since the conversion of the hydroxyl groups was not stoichiometrically achieved.

Table 1. Preparation of the Hyperbranched Polyimides

	M_w	M_n	PDI (M_w/M_n)	T_g (°C) [a]	T_5 (°C) [b]	T_{10} (°C) [b]
HB-PI-(OH)$_n$	133,800	8,300	16.2	278	536	561
HB-PSPI	255,900	11,000	23.3	266	404	517

[a] Temperatures of glass transition, determined by DSC at a heating rate of 10 °C/min in nitrogen; [b] Temperatures of 5 % (T_5) and 10 % (T_{10}) weight loss, determined by TGA at a heating rate of 20 °C/min in nitrogen.

Table 2. Elemental Analysis Results of the Hyperbranched Polyimides

	C (wt%)	H (wt%)	N (wt%)	F (wt%)	RM [a]	M_c [b]	n [c]
HB-PI-(OH)$_n$	59.95	3.20	4.16	17.44	0.47	11,218	10
HB-PSPI	61.22	3.34	3.80	15.35			

[a] molar ratios of TAPOB to 6FDA units in the polyimides, estimated according to the elemental analysis results; [b] average molecular weights of polyimides by calculation; [c] average numbers of terminal groups per polyimide molecule by calculation.

Polymer Properties

Figure 3 shows the thermogravimetric behaviors of HB-PI-(OH)$_n$ and HB-PSPI in nitrogen. Both of the polymers exhibited rather good thermal stability, having a temperature at 10% weight loss above 517 °C. Weight loss in the temperature range of 290-450 °C was observed for HB-PSPI, mainly due to the thermal decomposition of cinnamate groups. The weight loss in this region is approximately 7.5% (the calculated value of weight content for cinnamate groups is 5.7% according to the molar ratio obtained by ^{1}H NMR analysis). Values of T_g, T_5 and T_{10} of the two polymers were summarized in Table 1. As can be seen, the T_g of the polyimide decreased from 278 °C to 266 °C after the terminal modification of phenol groups to cinnamate groups. This may be caused by the decrease of the end-group polarity [3,16], and the introduction of the ester linkages at the periphery.

The hyperbranched photosensitive polyimide (HB-PSPI) exhibited an excellent organosolubility. A solution of HB-PSPI with over 10 wt % solid content can be obtained at room temperature in low boiling point solvents, such as acetone, 1,1,2-trichloroethane, THF and chloroform.
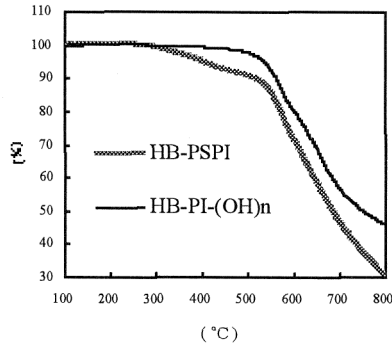

Figure 3. Thermogravimetric Curves of the Hyperbranched Polyimides Obtained in Nitrogen with a Heating Rate of 20 °C/min
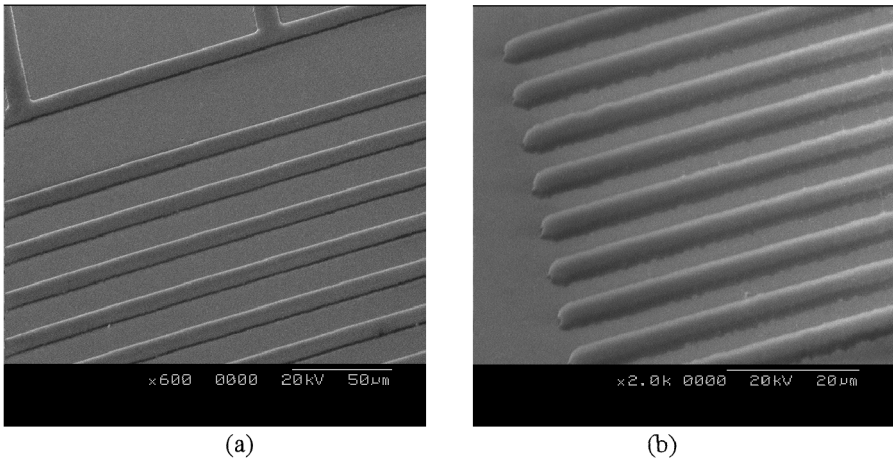

(a)   (b)

Figure 4. SEM Images of the Photolithographic Patterns of the Hyperbranched Photosensitive Polyimide *(a, _600, line width: 10 _m; b, _2000, line width: 3_m)*

Photolithographic Properties of Hyperbranched Photosensitive Polyimide (HB-PSPI)

To determine the photolithographic properties of HB-PSPI, thin films with a thickness of around 2 • m, containing 5 wt % (relative to HB-PSPI) Michler's ketone as the photosensitizer, were prepared by spin coating on clean glass substrates. After prebaked at 80 • C for 2 h, the films were exposed to UV radiation in a contact mode with a mask. The films were then immersed in a mixture of 1,1,2-trichloroethane/2-propanol (9/1, v/v) to remove the unexposed regions. After rinsed with 2-propanol and dried at 150 • C for 5 h, the patterns were observed by scanning electron microscopy (SEM). As can be seen in Figure 4, highly resolved line image with a line width of 10 • m was obtained (a). Well-defined line as thin as 3• m could be patterned, but the line edges were jagged and rounded (b). This is possibly due to the broad molecular weight distribution of the hyperbranched photosensitive polyimide. To achieve a more excellent resolution, a detailed optimization study is in progress, involving the improvement of the content of photosensitive cinnamate groups and the narrowing of its molecular weight distribution.

Conclusions

We have successfully prepared a kind of hyperbranched polyimide containing photosensitive cinnamate groups at the periphery, and demonstrated its good photolithographic property with a resolution greater than 3 • m. Efforts to improve the content of photosensitive cinnamate groups and narrow its molecular weight distribution are going on, aiming at further improving its patterning resolution and UV photosentivity.

References

1. Omote T (1996) Potosensitive Polyimides: Molecular Design and Synthesis. In: Ghosh MK, Mittal KL (ed) Polyimides-Fundamentals and Applications. Marcel Dekker, New York, P. 121
2. Bureau JM, Droguet JP (1996) Applications of Polyimides as Photosensitive Materials. In: Ghosh MK, Mittal KL (ed) Polyimides-Fundamentals and Applications. Marcel Dekker, New York, P.743
3. Kim YH (1998) J Polym Sci Part A: Polym Chem 36: 1685
4. Voit B (2000) J Polym Sci Part A: Polym Chem 38: 2505
5. Inoue K (2000) Prog Polym Sci 25:453
6. Jikei M, Kakimoto M (2001) Prog Polym Sci 26: 1233
7. Tomalia DA, Fréchet JMJ (2002) J Polym Sci Part A: Polym Chem 40: 2719
8. Tully DC, Wilder K, Fréchet JMJ, Trimble AR, Quate CF (1999) Adv Mater 11: 314
9. Trimble AR, Tully DC, Fréchet JMJ, Medeiros DR, Angelopoulos M (2000) Polym Preprint 41(1): 325
10. Tully DC, Trimble AR, Fréchet JMJ (2000) Adv Mater 12: 1118
11. Haba O, Haga K, Ueda M (1997) Polym Mater Sci Eng 77: 426
12. Okazaki M, Shibasaki Y, Ueda M (2001) Chem Lett 8: 762
13. Chen H, Yin J (2002) J Polym Sci Part A: Polym Chem 40: 3804
14. Berrada M, Carriere F, Coutin P, Monjol P, Sekiguchi H (1996) Chem Mater 8: 1029
15. Fang J, Kita H, Okamoto K (2000) Macromolecules 33: 4639
16. Kim Y, Beckerbauer R (1994) Macromolecules 27: 1968