Polymer Bulletin 50, 303–310 (2003)
DOI 10.1007/s00289-003-0181-9

Polymer Bulletin

Preparation of Auto-Photosensitive Hyperbranched Co-polyimide by the Condensation of 4,4'-(Hexafluoroisopropylidene)diphthalic Anhydride and 3,3',4,4'-Benzophenonetetracarboxylic Dianhydride with 1,3,5-Tris(4-aminophenoxy)benzene through a Stage Addition Reaction Method

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Received: 17 March 2003/Revised version: 8 May 2003/Accepted: 16 May 2003

Summary

An approach of stage addition copolymerization was adopted to further improve the organosolubility of the auto-photosensitive hyperbranched polyimide based on TAPOB-BTDA-2,6-dimethylaniline through the incorporation of 6FDA in the inner of macromolecular framework. In the first stage, the amino-terminated hyperbranched oligo(amic acid) was synthesized by the addition of 6FDA solution to TAPOB solution. Next, the oligomer, like a multi-amine monomer with core structure, was added dropwise to the solution of BTDA to give an anhydride-terminated co-poly(amic acid), which was then end-capped by 2,6-dimethylaniline. In the end, the precursor was chemically imidized to yield an auto-photosensitive hyperbranched 6FDA-TAPOB-BTDA-2,6-dimethylaniline-based co-polyimide with core-shell structure. The co-polyimide exhibited a great improvement in organosolubility (the solid content of the polymer solution increased from 8 wt% to over 15 wt% in NMP and DMF) compared to the polymer based on TAPOB-BTDA-2,6-dimethylaniline. The two polyimides showed similar thermal properties and photolithographic property, with a patterning resolution higher than 3 μm.

Introduction

Since the first intentional preparation of hyperbranched polymers by Kim [1] 15 years ago, research and development work on the dendritic macromolecules has been abundantly reported to the world [2-6]. Studies in this field include theory, synthesis, structural characterization, and chemical and physical properties. Hyperbranched polymers are usually prepared by the facile one-pot polymerization of AB_2-type monomers. A_2 + B_3-type monomer systems can also be adopted in the synthesis of hyperbranched polymers, which has the advantage of commercial availability of monomers. More interestingly, Yan et al [7,8] reported a new strategy to synthesize hyperbranched polymers. In the initial course of polymerization, an unsymmetrical

BB'_2 monomer and a A_2 monomer combined in situ quickly to yield a AB'_2 intermediate, which was then self-polymerized without the risk of gelation, like the AB_2 monomer systems.

In recent years, the explorations on hyperbranched polymers for practical applications have drawn considerable interests [3-5]. The facile one-pot polymerization is suitable for large scale industrial production, as makes them a very promising material candidate for industrial applications. Hyperbranched polymers can be used not only in the classical aspects as modifiers in epoxy composites [9], as crosslinking agents for high solid coatings or powder coatings [4,10,11], and as melt modifiers, additives, or blend component in polymer processing [4,12], but also in the fields of nano technology, optics and electronics, light emitting devices, sensors, and catalysis [3].

Besides, the applications of hyperbranched polymers as photoresist materials seem to be very promising [13-19]. Hyperbranched polymers with a compact molecular chain and low chain entanglement attribute may offer some advantages over linear polymers when attempting to pattern feature sizes that are on the order of the molecular dimensions. In addition, the peripheral location of the photosensitive groups at the polymer framework is expected to bring about high sensitivity toward exposure. Fréchet et al [13] developed a chemically amplified resist material, *t*-BOC resist, based on poly(benzylether) dendrimers with high sensitivity toward both DUV and e-beam irradiation, giving a reproducible patterning resolution well below 100nm. They also demonstrated the first example of the use of a hyperbranched polymer as a chemically amplified resist [14]. Recently, Ueda et al [17] reported a new negative-working photoresist based on resorcinol-terminated hyperbranched poly(ether imide), with 4,4'-methylenebis(2,6-bis(hydroxymethyl))phenol as a cross-linker and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate as a photoacid generator, which gave a feature resolution of 4.5 μm when exposed to 365 nm light. We reported a hyperbranched polyimide-based photoresist with excellent organosolubility and a patterning resolution greater than 3 μm upon 365 nm UV-exposure, which possessed the photosensitive cinnamate groups at the periphery [19].

Photosensitive polyimides have been widely used as protection and insulation layers in the field of semiconductor manufacturing. The usual photosensitive poly(amic acid) systems, which need thermal imidization after patterned, sometimes bring about difficulty in practical processing because of the high temperature and the substantial shrinkage of the film resulting from the removal of small molecules during thermal cyclization [20]. So, the fully imidized photosensitive polyimides, such as auto-photosensitive polyimides containing benzophenone and *ortho*-alkyl groups, are desired to overcome these problems [21]. In our previous work [22], a series of auto-photosensitive hyperbranched polyimides based on 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 1,3,5-tris(4-aminophenoxy)benzene (TAPOB) were synthesized via in situ end-capping of the terminal anhydride groups of the anhydride-terminated hyperbranched poly(amic acid) precursors with *ortho*-alkyl aniline, which were then chemically imidized. Although the resulting polymers were soluble in strong polar solvents, the solid contents of polymer solutions were limited, lower than 8 wt% in NMP. In this paper, an approach of copolymerization was adopted to further improve the solid contents of polymer solution. In the first stage, the amino-terminated hyperbranched oligo(amic acid) was synthesized by the addition of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) solution to TAPOB solution. Next, the oligomer, like a multi-amine monomer with core structure, was added dropwise to the solution of BTDA to give an anhydride-terminated co-poly(amic acid), which was then end-capped in situ by 2,6-dimethylaniline. In the end, the precursor was chemically imidized to yield an auto-photosensitive hyperbranched co-polyimide with core-shell structure.

Experimental

Chemicals

N-Methyl-2-pyrrolidone (NMP) was distilled from calcium hydride under reduced pressure. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) were obtained commercially, and purified by recrystallization from acetic anhydride before use. 1,3,5-Tris(4-aminophenoxy)benzene (TAPOB) was synthesized in our lab [23]. Other solvents and reagents were used as received.

Measurements

Infrared spectra (IR), UV-vis spectra, differential scanning calorimetric curves (DSC, at a heating rate of 10 °C/min in nitrogen) and thermogravimetric curves (TGA, at a heating rate of 20 °C/min in nitrogen) were recorded on FTIR Paragon 1000, Lambda 20/2.0, DSC Pyris 1 and TGA-7 of Perkin-Elmer, respectively. ^{1}H NMR analysis was 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 *N,N*-dimethylformamide (DMF) containing 0.01 mol/L lithium bromide with a flow rate of 1.0 mL/min at 70 °C. Polymer solutions were filtered through a Whatman 0.45 μm polytetrafluoroethylene (PTFE) filter before injected into the column. The polyimide patterning profiles were obtained with a Hitachi S-2150 scanning electron microscope (SEM). The samples were homogeneously coated with a very thin layer of gold using a SEM coating unit prior to analysis.

Synthesis of Auto-Photosensitive Hyperbranched Co-Polyimide (Scheme 1)

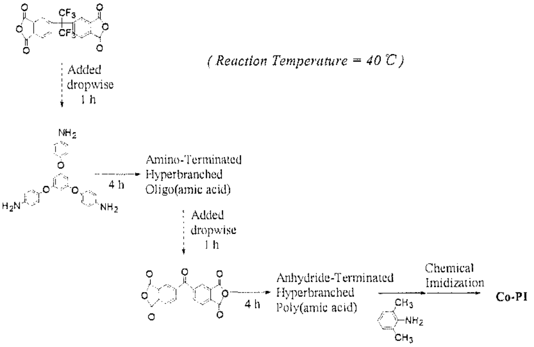
In a 150 mL thoroughly dried three-neck flask equipped with a nitrogen inlet and a magnetic stirrer, 5.5 mmol of TAPOB was dissolved in 30 mL of NMP. 5 mmol of 6FDA in 30 mL of NMP was dropwise added to the mixture through a syringe over 1 h at 40 °C. After another 4 h, the reaction was stopped. Then, the reaction mixture was added dropwise over 1 h at 40 °C to a 150 mL thoroughly dried three-neck flask containing 6.5 mmol of BTDA in 30 mL of NMP under nitrogen atmosphere and magnetic stirring. An excess amount of 2,6-dimethylaniline was added to the reaction system in a dark cabin 4 h later, and the reaction was further conducted for 5 h at 40 °C. Subsequently, 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 1000 mL ethanol. The polymer was collected by filtration and dried *in vacuo* without light exposure at 80°C for 24 h.

Photolithography of the Auto-Photosensitive Hyperbranched Co-Polyimide

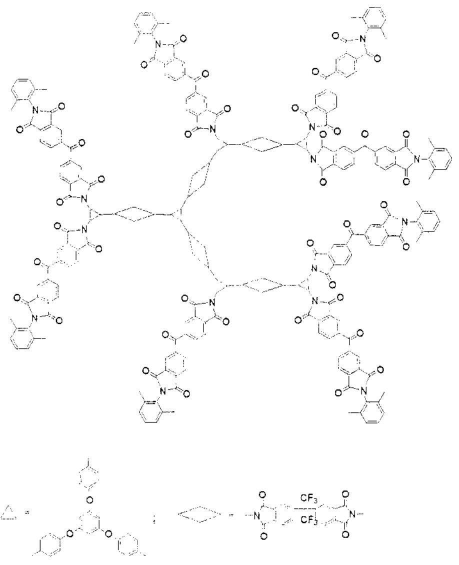
The auto-photosensitive hyperbranched co-polyimide was dissolved in NMP at a solid content of 10 wt %. The solutions were filtered through a 0.45 μm PTFE filter under pressure. The films were prepared by spin coating on clean glass substrates, and prebaked at 80 °C for 30 minutes. The thickness of the films was around 2 μm. The photoresist films were exposed in the contact mode with a mask to a 250 W high pressure mercury lamp for 5 min, which delivered a UV dose of 5.5 mJ/s with the strongest emission at 365 nm. The films were then developed in NMP at 50°C for 60 seconds and rinsed with 2-propanol. After development, the patterns were dried at 150 °C for 5 h, and evaluated by scanning electron microscopy (SEM).

Results and Discussion

Polymerization



Scheme 1. Synthesis of the Auto-Photosensitive Hyperbranched Co-Polyimide



Scheme 2. Chemical Structure for the Auto-Photosensitive Hyperbranched Co-Polyimide

The condensation of a diandydride and a triamine with different addition methods and monomer molar ratios led to anhydride-terminated or amino-terminated hyperbranched polyimides. When the triamine solution was added to the dianhydride solution with the monomer molar ratio of 1:2 (triamine : dianhydride), anhydride-terminated hyperbranched polyimide was obtained, whereas the addition of the dianhydride solution to the triamine solution with the molar ratio of 1:1 yielded amino-terminated one. In our previous work [23], a series of hyperbranched polyimides based on 1,3,5-tris(4-aminophenoxy)benzene (TAPOB) and conventional dianhydrides were prepared. The degrees of branching (DBs) were estimated by ^{1}H NMR analysis with the help of three model compounds, which represented linear unit, dendritic unit and terminal unit, respectively. The amino-terminated hyperbranched polyimides had DBs in the range of 0.62-0.67, while the anhydride-terminated or end-capped hyperbranched polyimides gave a DB value of 1. In the present work, a stage addition reaction method was adopted to prepare the hyperbranched co-polyimide (Scheme 1). In the first stage, the amino-terminated hyperbranched oligo(amic acid) was synthesized by the addition of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) solution to TAPOB solution. Next, the oligomer, like a multi-amine monomer with core structure, was added to the solution of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) to give an anhydride-terminated co-poly(amic acid), which was then end-capped in situ by 2,6-dimethylaniline. In the end, the precursor was chemically imidized to yield an auto-photosensitive hyperbranched co-polyimide with core-shell structure (Scheme 2).

As shown in Scheme 1, a solution of 6FDA was dropwise added over 1 h into the reaction system containing TAPOB in NMP with a dose of 5 mmol/5.5 mmol to afford an amino-terminated hyperbranched oligo(amic acid). The molar quantity of the unreacted amino groups at the periphery of the oligomer molecules can be calculated to be $(5.5\times3)-(5\times2)=6.5$ mmol. So, the multi-amine-monomer-like oligomer was added slowly enough to react with 6.5 mmol of BTDA in NMP to yield an anhydride-terminated hyperbranched co-poly(amic acid) precursor. Then, an excess amount of 2,6-dimethylaniline was used to end-cap the terminal anhydride groups of the precursor. The precursor was successively imidized chemically to afford the auto-photosensitive hyperbranched co-polyimide (Co-PI).

The structure of the auto-photosensitive hyperbranched co-polyimide was characterized by IR and ^{1}H NMR analyses. From IR analysis, the characteristic bands for imide structure were observed at 1783, 1725, 1370 and 722 cm^{-1} [19,23]; the peak at 1674 cm^{-1} displayed the presence of the carbonyl groups of benzophenone structure [24,25]; the absence of the absorption band around 1859 cm^{-1}, which is the characteristic absorption wavelength of the C=O stretching from the anhydride groups, indicates that the end-capping of the terminal anhydride groups by 2,6-dimethylaniline was achieved completely. In the ^{1}H NMR spectrum (Figure 1), the bands in the range of 7.7-8.3 ppm correspond to the resonance absorption of the phenyl hydrogen **d**, **e**, **f**, **g**, **h**, **i**, **j** and **k** of 6FDA, BTDA and 2,6-dimethylaniline residues, and the bands at around 7.25 ppm and 7.45 ppm can be attributed to the outer phenyl hydrogen **b** and **c** of the TAPOB residues, respectively, and the broad peak at around 6.55 ppm is from the absorption of the inner phenyl hydrogen **a** of the TAPOB residues [23]. The hydrogen resonance absorption of the *ortho*-methyl groups **L** can be found at around 2.15 ppm [26]. By comparison of the integration of the peaks of the hydrogen **a** and **L**, the molar ratio of the TAPOB residues to the end-capping groups can be estimated to be about 0.81.

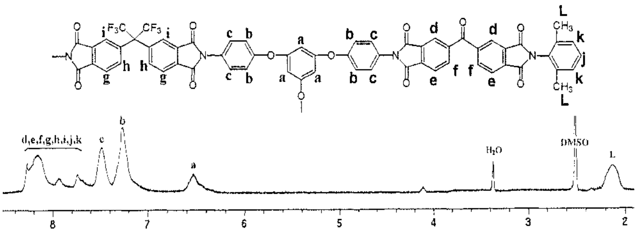


Figure 1. ^{1}H NMR Analysis of the Auto-Photosensitive Hyperbranched Co-Polyimide

Table 1. Preparation of the Auto-Photosensitive Hyperbranched Co-Polyimide

M_n	M_w	PDI (M_w/M_n)	T_5 (°C)	T_{10} (°C)	T_g (°C)
9,600	43,900	4.6	544	573	228

Table 2. Elemental Analysis Results of the Auto-Photosensitive Hyperbranched Co-Polyimide

C (wt%)	H (wt%)	N (wt%)	F (wt%)	O (wt%)	Ratio of Momomer Residues 6FDA/TAPOB/BTDA
67.90	3.09	4.69	8.21	16.11	1/1.12/1.33

The molecular weight of the auto-photosensitive hyperbranched co-polyimide was determined by gel permeation chromatography (GPC) using *N,N*-dimethylformamide (DMF) containing 0.01 mol/L lithium bromide as the eluant on the basis of linear polystyrene standards. As shown in Table 1, the polymer had a moderate molecular weight, $M_w = 43{,}900$ and $M_n = 9{,}600$, with a polydispersity index of 4.6. This attribute meets the characteristics of broad molecular weight distribution for the hyperbranched polymers from $A_2 + B_3$-type monomer systems [5,27].

The elemental analysis was performed to estimate the contents of 6FDA, TAPOB and BTDA residues in the auto-photosensitive hyperbranched co-polyimide (Table 2). Since the end-capping of the terminal anhydride groups was achieved completely as proved by the IR analysis, it is reasonable that one 6FDA residue contains two N, four O and six F, and one BTDA residue two N and five O, and one TAPOB residue bears three O. Thus, the molar ratio of the monomer residues 6FDA/TAPOB/BTDA in the co-polyimide can be calculated to be 1/1.12/1.33 according to the contents of F, N and O. The estimated average molecular weight of the co-polyimide on the basis of the molar ratio value is around 15,000, in agreement with the results from GPC analysis. The average number of the end groups per polyimide macromolecule can be deduced to be approximately around 14.

Polymer Properties

Thermal stability of the auto-photosensitive hyperbranched co-polyimide was characterized by thermogravimetry. The co-polyimide exhibited excellent thermal property, with a 5% weight loss temperature (T_5) at 544 °C and a 10% weight (T_{10}) temperature at 573 °C (Table 1). Under 450 °C, only trace of weight loss (c.a. 1 wt%) was observed. Differential scanning calorimetric analysis (DSC) revealed the glass transition temperature (T_g) of the co-polyimide at 228 °C. The thermal properties of the co-polyimide are rather similar to those of the auto-photosensitive hyperbranched polyimide based on BTDA-TAPOB-2,6-dimethylaniline (PI_2) [22].

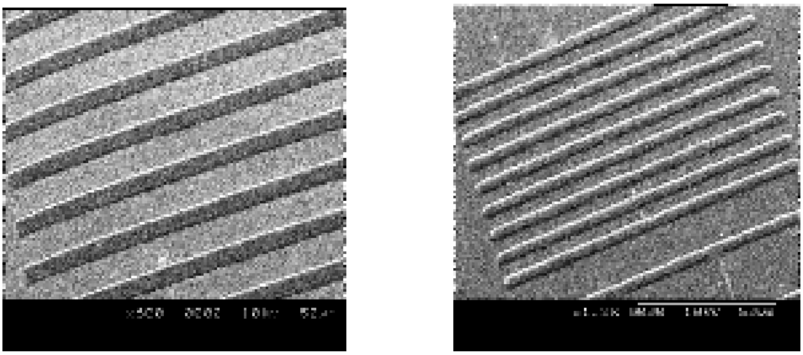
Table 3. Solubility of the Auto-Photosensitive Hyperbranched Co-Polyimide [a]

	NMP	DMF	DMSO	1,1,2-Trichloroethane	Chloroform	THF	Methanol
Co-PI[b]	++	++	++	++	++	+	-
PI$_2$[c]	++	++	++	+	+	-	-

[a] ++ = soluble; + = partially soluble; - = insoluble.

[b] hyperbranched co-polyimide based on 6FDA-TAPOB-BTDA-2,6-methylaniline.

[c] hyperbranched polyimide based on TAPOB-BTDA-2,6-methylaniline [22].



(a) (b)

Figure 2. Scanning Electron Micrographs of the Paterns from the Auto-Photosensitive Hyperbranched Co-Polyimide (a: × 300, Line Width = 10 μm; b: × 1000, Line Width = 3 μm)

The organosolubility of the auto-photosensitive hyperbranched 6FDA-TAPOB-BTDA-2,6-methylaniline-based co-polyimide (Co-PI), which was evaluated with 20 mg of polymers in 1 mL of solvents (2 wt%), was summarized in Table 3, taking the auto-photosensitive hyperbranched polyimide based on TAPOB-BTDA-2,6-dimethylaniline (PI$_2$) [22] as a comparison. Co-PI showed better solubility in the solvents detected compared to PI$_2$. Especially, the solid content of Co-PI in NMP or DMF can reach more than 15 wt%, much higher than those of PI$_2$ (c.a. 8 wt%). The incorporation of 6FDA in the inner of the macromolecular framework contributes to the improvement in organosolubility (6FDA-based polyimides are well-known characteristic of excellent organosolubility).

Photolithographic Property

The polyimides containing benzophenone and *ortho*-alkyl groups are inherently photosensitive, for the mechanism that triplet benzophenone moieties undergo hydrogen abstraction from a spatially adjacent *ortho*-benzyl-positioned alkyl hydrogen of the diamine moieties and successively the formation of radical coupling to yield a crosslink structure [21,28].

The patterning procedure, which was developed in our previous work [22], was used. Thin films of the auto-photosensitive hyperbranched co-polyimide with a thickness of around 2 μm were prepared by spin coating on clean glass substrates, and prebaked at 80 °C for 30 minutes before exposed to UV irradiation with the strongest emission at 365 nm in a contact mode with a mask; NMP at 50 °C was used as the developing solvent, and 2-propanol as rinsing solvent. The scanning electron micrographs in Figure 5 demonstrated a highly resolved image with a line width of 6 μm (a); and a well-defined image with lines as thin as 3 μm, although the lines were jagged at the edges (b), as was also observed in the patterns originating from TAPOB-BTDA-2,6-methylaniline-based PI_2 [22]. Studies on the evaluation and comparison of the photosensitivity of co-polyimide and PI_2 upon UV-exposure are under way.

Conclusion

A kind of auto-photosensitive hyperbranched co-polyimide based on 6FDA-TAPOB-BTDA-2,6-dimethylaniline was successfully prepared through a stage addition copolymerization method. The resulting polymer exhibited a great improvement in organosolubility (the solid content of polymer solution increased from 8 wt% to over 15 wt% in NMP and DMF) compared to the auto-photosensitive hyperbranched polyimide from TAPOB-BTDA-2,6-dimethylaniline. The two polyimides showed similar thermal properties and photolithographic property, with a patterning resolution higher than 3 μm. Optimization investigations on their photolithographic properties and photosensitivity are going on.

Acknowledgements. The authors would like to express their gratitude to the Ministry of Education of China ("Kuashiji" Scholar Project) and Science & Technology Commission of Shanghai Government (011661084) for their financial support.

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