

Synthesis and Characterizations of Positive-Working Photosensitive Polyimides Having 4,5-Dimethoxy-*o*-Nitrobenzyl Side Group

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To synthesize a new positive-working photosensitive polyimide, alkali-soluble polyimide containing carboxylic acid side group was synthesized, and parts of its carboxylic acid groups were esterified with 4,5-dimethoxy-2-nitrobenzyl bromide. The chemical structure of the resulting polymer was characterized by ¹H-NMR and FT-IR spectroscopies. The substitution ratio of photosensitive groups was estimated by ¹H-NMR integration values, and the thermal properties were examined by differential scanning calorimetry and thermogravimetric analyses. Upon UV irradiation, 4,5-dimethoxy-2-nitrobenzyl moiety underwent the photodegradation with generation of carboxylic acid side groups as evidenced by UV/vis spectroscopy. As a result, the polymer became soluble in alkaline developer, and a micron-sized positive pattern was successfully fabricated from the synthesized polymer.

Key Words : Photosensitive, Polyimides, Positive-working, Photoresist, *o*-Nitrobenzyl

Introduction

Polyimide has been used in aerospace and microelectronics industries as an important material due to its excellent thermal properties, decent processibility, good mechanical strength, and low dielectric property.¹ Since 1970s, it has been used widely as an electrically insulating film or coating material in electronics area such as fabrication of transistors, liquid crystal display devices, printer parts, integrated circuits, printed circuit boards, encapsulants, and inter-layer dielectrics.²⁻⁷ Because most polyimides are insoluble and intractable, thin polyimide film is prepared by the thermal imidization of soluble precursor, poly(amic acid) (PAA) after spin-coating on a substrate. In addition to this, lithographic process using a photoresist is required to produce a micro-patterned polyimide which is essential in semiconductor fabrication. Recently, photosensitive polyimides (PSPIs) have attracted a great attention because they can reduce processing steps significantly.⁸⁻¹⁰ Initially, the most widely investigated are the negative-working PSPIs, in which the UV-exposed part becomes insoluble *via* photocrosslinking or photo-polymerization reaction, while the unexposed part remains soluble in developing solution. More recently, these negative-working PSPIs have been replaced by the positive-working PSPIs because of several reasons. Firstly, since only the area to be removed is exposed in the positive-working lithographic process, there is less chance of process error originating from the contaminants such as dust. Secondly, solubility difference between the exposed and unexposed parts is not large enough in the negative-working PSPIs resulting in micro-patterns of lower resolutions or low thickness profiles. Additionally, positive-working PSPIs can be designed to be soluble in alkaline developers such as an aqueous solution of tetramethylammonium hydroxide (TMAH) which is preferred in the

industry.

The first positive-working PSPI was reported by Kubota and his coworkers.¹¹⁻¹³ They reported the synthesis of poly(amic acid *o*-nitrobenzyl ester), in which *o*-nitrobenzyl ester decomposes to the corresponding carboxylic acid and *o*-nitrosobenzaldehyde upon UV irradiation.¹⁴ Upon exposure to UV light, the poly(amic acid *o*-nitrobenzyl ester) was converted to PAA which is soluble in alkaline developer. In this system, however, there were some drawbacks such as synthetic difficulties and limited sensitivity only to deep UV. Since then, several groups have reported positive-working PSPI systems based on various photo-functional groups including *o*-diazonaphthoquinone (DNQ),¹⁵ 1,4-dihydropyridine derivatives,¹⁶ and diphenyliodonium 5-hydroxynaphthalene-1-sulfonates.¹⁷ These PAA-based systems also have inherent problems such as high solubility of unexposed part in alkaline developer leading to a significant thickness loss during the developing process, poor storage stability, and large volume shrinkage during the conversion of amic acid to imide unit.¹⁸ To overcome these problems, PSPIs of fully imidized type have been investigated by several workers. UV-decomposable polyimide from oxydianiline (ODA) and cyclobutane tetracarboxylic dianhydride was reported by Moore and his coworkers.¹⁹ More recently, PSPIs based on polyhydroxyimide (PHI) having various photo-functional groups such as dispersed DNQ,²⁰ covalently bonded *t*-butoxycarbonyl (*t*-BOC)²¹ or *o*-nitrobenzyl moieties^{22,23} have been reported. Hydroxy-functionalized aromatic polyimides were used in these systems for the solubilization of polymer backbone in alkaline developers. Photo-activated deprotection of *t*-BOC or *o*-nitrobenzyl moieties results in soluble PHI.

Recently, we reported a new type of positive-working PSPI consisting of poly[imide-*co*-(4,5-dimethoxy-2-nitrobenzyl amic ester)] (DMNB-PIAE).¹⁸ Upon UV irradiation,

4,5-dimethoxy-2-nitrobenzyl (DMNB) moiety undergoes the photo-degradation. As a result, the polymer becomes soluble in alkaline developer due to the formation of carboxylic acid moiety, which was used to produce micron-sized positive patterns. In this system, better storage stability can be achieved due to the lack of unstable amic acid moiety. By introducing 4,5-dimethoxy groups, absorption wavelength of *o*-nitrobenzyl moiety was shifted to 350 nm from 250-300 nm where the overlapping of internal absorption of polyimide backbone could occur. Sensitivity and contrast were estimated to be 4000-6000 mJ/cm², and 3.1-4.9, respectively, depending on the content of DMNB groups. However, the decomposed product of DMNB were found to act as an internal UV filter absorbing light required for DMNB decomposition. As a result, degree of DMNB photoreaction was limited to less than about 30%.

As an extension of these works, we report a novel positive-working PSPI based on alkali-soluble polyimide containing photosensitive DMNB groups. In this work, aromatic polyimide (PI-CA) with carboxylic acid side group was prepared firstly from 3,5-diaminobenzoic acid (DABA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). PI-CA was soluble in most of aqueous alkaline developers due to the carboxylic acid groups. Then, parts of carboxylic acids were esterified with 4,5-dimethoxy-2-nitrobenzyl bromide (DMNBBr) in the presence of 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU) to yield a new positive-working photosensitive polyimide (PI-DMNB) as shown in Scheme 1. As far as we understand, the utilization of carboxylic acid-functionalized aromatic polyimide for the preparation of positive-working PSPI has never been reported. The novel PSPI system reported in this work has many advantages such as straightforward synthesis, ease of controlling the substitution degree, high sensitivity, and minimized volume shrinkage owing to a fully-imidized polyimide structure.

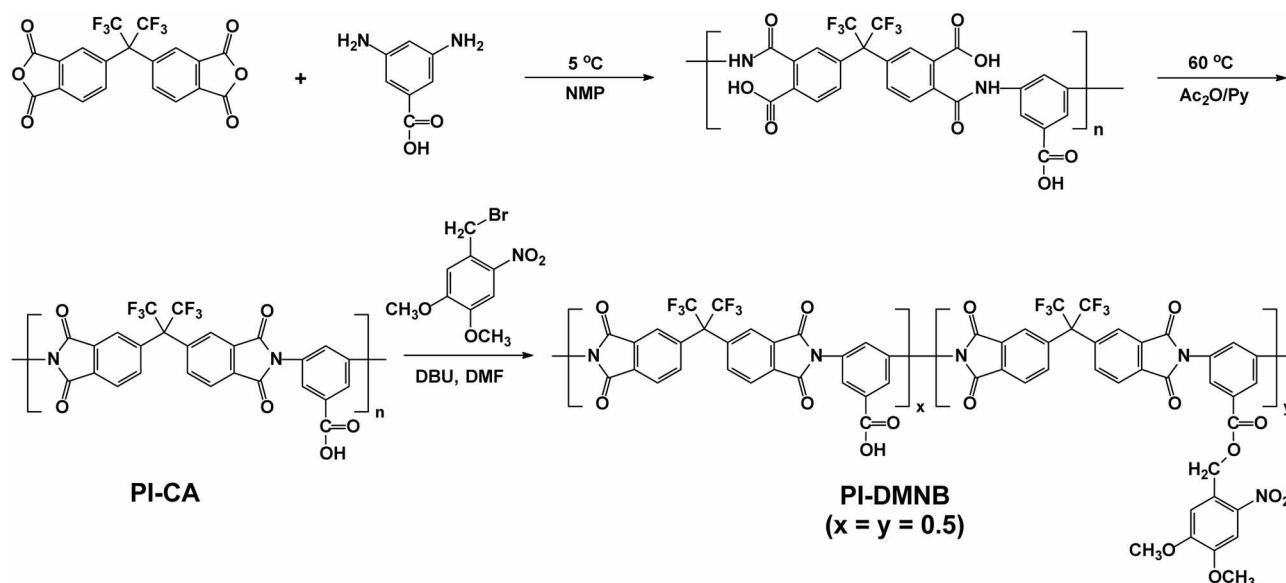
Experimentals

Reagents. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), 3,5-diaminobenzoic acid (3,5-DABA), DMNBBr, and DBU were purchased from Aldrich Chemical Co., and used without further purification. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), pyridine and acetic anhydride were used after stirring with CaH₂ for 24 h with subsequent distillation under reduced pressure.

Synthesis of carboxylic acid-functionalized polyimide (PI-CA). In 100 mL round-bottom flask, 1.027 g of 3,5-DABA (6.757 mmol) was dissolved in 15 mL of NMP. To this solution, was added 3 g of 6FDA (6.757 mmol) and 30 mL of NMP. The reaction mixture was stirred under N₂ atmosphere for 24 hr in ice-water bath to obtain carboxylic acid-functionalized poly(amic acid) (PA-CA). To PA-CA solution, 3.263 mL of pyridine (40.54 mmol) and 3.832 mL of acetic anhydride (40.54 mmol) was added, and chemical imidization was performed by stirring the mixture at 60 °C for 6 h. After cooling to room temperature, the reaction mixture was reprecipitated into water, and the precipitate was washed with methanol repeatedly. As white fibrous solid, carboxylic acid-functionalized polyimide (PI-CA) was obtained after drying in vacuum oven for 24 hr.

¹H-NMR (400 MHz, DMSO-*d*₆): 7-8.5 ppm (aromatic protons of 6FDA and 3,5-DABA, m), 11-12 ppm (-COOH, s).

Synthesis of photosensitive polyimide (PI-DMNB). Carboxylic acid groups in PI-CA can be esterified up to ca. 70 mol% by using 4,5-dimethoxy-2-nitrobenzyl bromide (DNMB). In this work, however, only 50 mol% of carboxylic acid group was reacted with DNMB for evaluation of this PSPI system. Typical procedure for the synthesis of PI-DMNB is as follows: 1 g of PI-CA was dissolved in 6 mL of DMF, and 0.116 g of DMNB (50 mol% to carboxylic acid groups) and 0.543 g of DBU (2 mol equivalent to DMNB)



Scheme 1. Synthetic diagram of photosensitive polyimide, PI-DMNB.

were added. The mixture was stirred for 24 h at 60 °C under N₂ atmosphere, and poured into water to obtain crude PI-DMNB as light yellow powder. The solid was dissolved in DMF, and reprecipitated into methanol for twice.

¹H-NMR (400 MHz, DMSO-d₆): 7-8.5 ppm (aromatic protons of 6FDA, 3,5-DABA, and DMNB, m), 3.8 ppm (CH₃-O-, m), 5.7 ppm (-OCH₂-Ph, s).

Instruments and patterning experiments. Fourier transform infrared (FT-IR) spectra were obtained with JASCO Model 300E FT-IR spectrometer. ¹H-NMR (400 MHz) was recorded with a JEOL Model 400 spectrometer. DMSO-d₆ was used as a solvent, and chemical shifts were reported in ppm unit with tetramethylsilane (TMS) internal reference. The UV/vis spectra were measured on a Scinco Model UV-3100S. GPC experiment was performed by a Waters Model 2690 with THF as an eluent and polystyrene standard for calibration. In order to study glass transition temperature (T_g) and thermal behavior of polymers, differential scanning calorimetry (DSC) was performed on DSC 2010 (TA Instruments) under nitrogen flow (20 cm³/min) at a heating rate of 10 °C/min with the sample weight of about 5-10 mg. Thermogravimetric analyses (TGA) were carried out on TGA 2050 (TA Instruments) under nitrogen atmosphere at a heating rate of 10 °C/min up to 700 °C.

For UV/visible spectroscopic and photosensitivity experiments, polymer films were prepared from DMF solution (ca. 15 wt.-%) by spin-casting onto glass or quartz plates. After removal of solvent by heating at 90 °C for 5-20 min, the polymer films were irradiated with a high pressure mercury lamp (Nanotec NT-HG1K-V09-SOR UV lamp) with an intensity of 90 mW/cm² for different time intervals. Line-and-space photomask pattern was used for lithographic experiments in contact printing exposure mode. The exposed film was developed in 2.38% aqueous tetramethylamine hydroxide (TMAH) solution for 1 min at 20 °C. The resulting pattern was examined by using optical microscope (Nikon ECLIPSE E600POL) and scanning electron microscope (SEM JEOL JSM 5800).

Results and Discussion

Synthesis of PI-DMNB. The polymer structure and synthetic scheme of photosensitive polyimide were illustrated in Scheme 1. In the most of previous works, polyhydroxyimide (PHI) had been used as a base-soluble polyimide backbone for the preparation of positive-working PSPI.²¹⁻²³ However, in this work, we employed 3,5-diamino benzoic acid (3,5-DABA), a carboxylic acid-functionalized diamine monomer and 6FDA. These monomer pair provided an alkaline-soluble polyimide (PI-CA) with minimum absorption at > 350 nm. The esterification of carboxylic acid groups by DMNB was achieved in the presence of DBU. In Figure 1, ¹H-NMR spectra of PI-CA and PI-DMNB were depicted. Protons corresponding to aromatic rings of 6FDA, 3,5-DABA, and DMNB were observed at 6.5-8.5 ppm. Benzylic protons and methoxy protons of DMNB were found at 5.7 and 3.8 ppm, respectively. Proton corresponding to carbox-

ylic acid was observed at 11.0 ppm. The substitution degree was estimated from the integration values of protons corresponding to aromatic rings of 6FDA, 3,5-DABA, and DMNB (6.5-8.5 ppm) and methoxy group (3.8 ppm). The esterification reaction was almost quantitative up to 50 mol%. However, slight decrease of substitution degree was observed for higher DMNBBr amounts (> 60 mol%). Maximum substitution degree of 68% was obtained when 75 mol% of DMNBBr was used. In this work, polyimide of 50 mol% substitution degree was used to investigate its photo-patterning behavior. From FT-IR spectra (Fig. 2), the polymer structures were also confirmed. Characteristic two imide carbonyl stretching of PI-CA and PI-DMNB were found at 1781, and 1730 cm⁻¹. Stretching vibration of nitro group was observed at 1520, 1330 and 770 cm⁻¹.

The solubility of PI-CA and PI-DMNB was summarized in Table 1. Either PI-CA or PI-DMNB was soluble in THF, acetone and aprotic polar solvents such as DMF, DMAc, DMSO, and NMP. As expected, PI-CA was soluble in alkali whilst PI-DMNB was not. DMF solution was used to spin-cast the polymer, and the film forming ability was practically good compared to other soluble polyimides.

To investigate thermal stability of PI-CA and PI-DMNB, both samples were subjected to thermogravimetric analyses (TGA). As shown in Figure 3, small weight decrease (~0.9 wt.%) for PI-CA sample was observed from 130 °C to 191

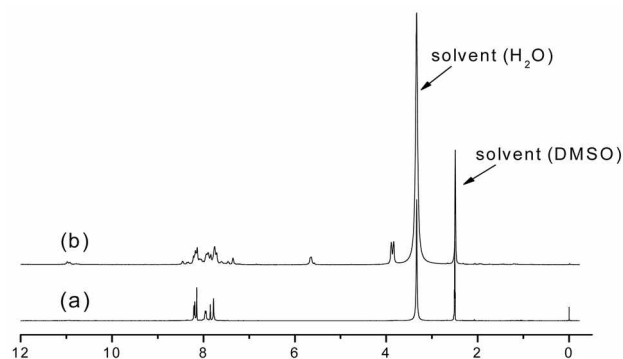


Figure 1. ¹H-NMR spectra of (a) PI-CA and (b) PI-DMNB.

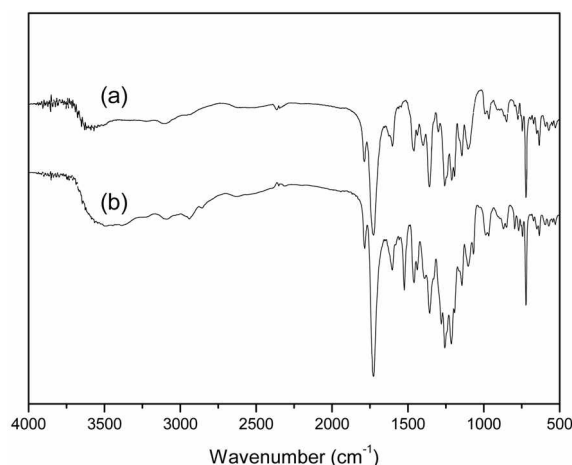
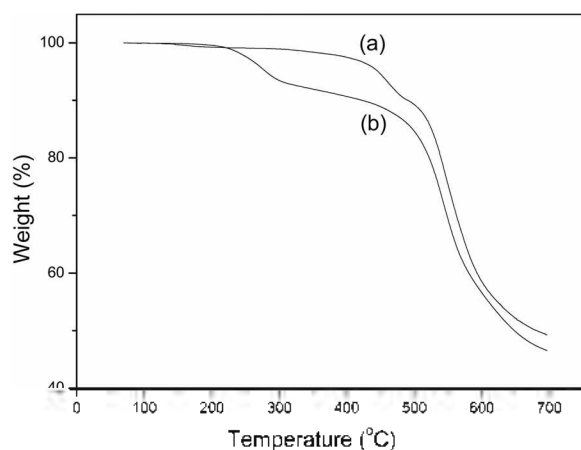
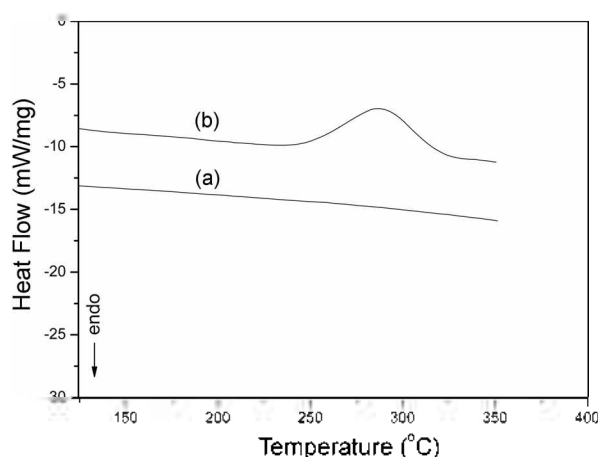


Figure 2. FT-IR spectra of (a) PI-CA and (b) PI-DMNB.

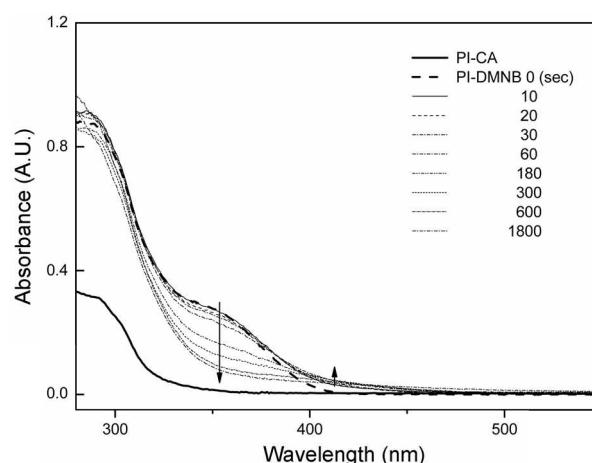
Table 1. Solubility of PI-CA and PI-DMNB

Sample	PI-CA	PI-DMNB
DMSO	☉	☉
DMAc	☉	☉
DMF	☉	☉
THF	☉	☉
Acetone	☉	◐
EA	☉	◐
1 wt% aq. NaOH	☉	●
Xylene	●	●
CHCl ₃	●	●
MeOH	●	●
Toluene	●	●
MC	●	●
Cyclohexanone	●	●

☉: soluble; ◐: partially soluble; ●: insoluble

**Figure 3.** TGA curves of (a) PI-CA and (b) PI-DMNB.**Figure 4.** DSC curves of (a) PI-CA and (b) PI-DMNB.

°C probably due to slightly incomplete imidization and/or residual solvent (NMP). Then, two-step decomposition was observed. The first gradual decomposition was detected at 272 °C, and the decomposition continued up to 482 °C, which was seemingly attributed to the decomposition of carboxylic acid side groups. The weight loss of this decom-

**Figure 5.** UV spectral change of PI-CA and PI-DMNB films during UV exposure.

position was estimated to be *ca.* 9.1% close to the theoretical weight loss of carboxylic acid (*ca.* 7.5%). Main chain decomposition of PI-CA was observed at higher than 500 °C with fast weight loss. In the case of PI-DMNB, the fast decomposition was observed at 215 °C, which is ascribed to the decomposition of DMNB, followed by slow decomposition of carboxylic acid side groups from 304 °C to 482 °C. Total weight loss at 482 °C was estimated to be about 13.5%, and the theoretical weight loss was calculated to be 18.8%. It was suggested that part of decomposed products is incorporated in the residual mass at high temperature. Differential scanning calorimetry (DSC) was also performed for both PI-CA and PI-DMNB. For PI-CA, no appreciable peak was found up to 350 °C. However, in the case of PI-DMNB, exothermic peak due to thermal decomposition was observed at 230 °C. For both of samples, no glass transition temperature was detected up to 230 °C.

Photosensitive properties. UV spectral change (in Figure 5) was recorded with respect to the UV irradiation time for both PI-CA and PI-DMNB films coated on a quartz plate. Compared to that PI-CA sample is almost colorless showing no absorption at longer than 350 nm, PI-DMNB has pale yellow color with characteristic absorption at 352 nm. This peak gradually decreased with UV exposure, which is attributed to the photo-induced decomposition of 4,5-dimethoxy-2-nitrobenzyl groups with generation of carboxylic acid moiety in the polymer structure. Slight increase of absorption tail at around 406 nm was also observed probably due to the decomposed product of DMNB group. The absorption coefficient of this band was relatively small compared to that of DMNB. It was concluded that this does not interfere with the photo-decomposition of DMNB groups. The rate of decomposition showed exponential decay curve as illustrated in Figure 6 where absorbance at 351 nm was plotted against exposure time. In our previous research using amic acid-type PSPI modified with DMNB moiety,¹⁸ the decomposed product of DMNB acted as an internal UV filter blocking UV light from being absorbed by DMNB groups. As a result, maximum of 32.5% DMNB group could be

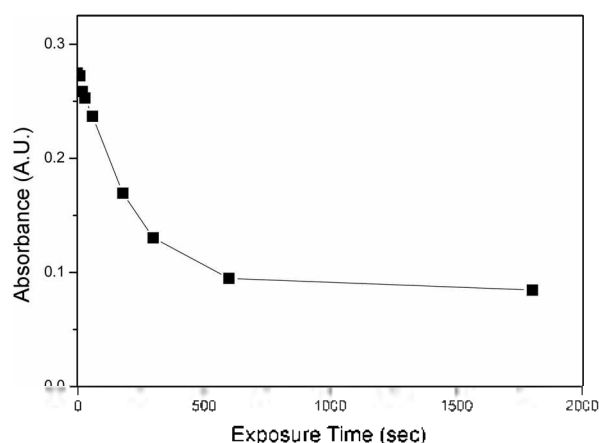


Figure 6. Change of absorbance at 351 nm for PI-DMNB during UV exposure.

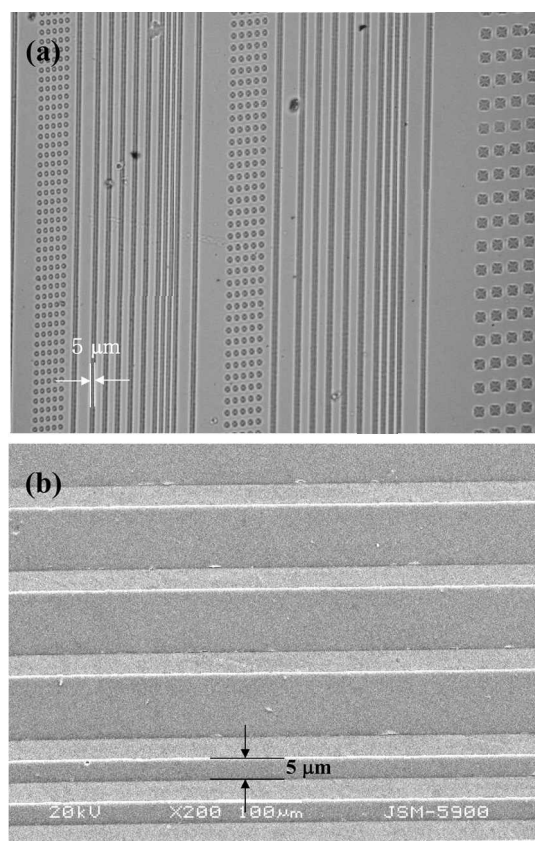


Figure 7. (a) Optical microscopic image and (b) scanning electron microscopic image of line-and-space patterns obtained from PI-DMNB.

decomposed even after a prolonged period of exposure time. In the present study, however, almost 70% of DMNB was decomposed in 10 min as estimated from the absorbance change.

Lithographic evaluation. To investigate photo-patterning property of PI-DMNB, we preliminarily attempted to perform lithographic experiments by using line-and-space mask pattern with contact printing mode. After spin-coating PI-DMNB solution on a glass substrate, the sample was pre-

baked for 5 min at 90 °C to remove solvent. The thickness of resulting film was measured to be ca. 5 μm. In this work, no other components such as a photoinitiator or dissolution inhibitors were required, since our polymer system is intrinsically photosensitive. After UV exposure for 60 sec (1500 mJ/cm²), the substrate was developed with 2.38 wt.% aqueous TMAH for 60 sec at 20 °C. The resulting pattern was examined by optical microscope and SEM as shown in Figure 7. The maximum resolution obtained by this experiment was 10 μm with 5 μm thickness. More work should be required to optimize photosensitivity and other lithographic properties by selectively changing the monomer structure and/or degree of substitution as well as the lithographic conditions. Considering the system has not been optimized, however, the above results clearly show that the newly designed polyimide structure is promising for the development of positive-working PSPI system.

Conclusion

A new positive-working photosensitive polyimide system was developed based on carboxylic acid-functionalized polyimide containing 4,5-dimethoxy-2-nitrobenzyl ester as a photosensitive side group. Firstly, base-soluble polyimide was synthesized from 3,5-diaminobenzoic acid and 4,4'-(hexafluoroisopropylidene) anhydride. Then, part of carboxylic acids was esterified with 4,5-dimethoxy-2-nitrobenzyl bromide. The structure and thermal property of resulting polymer were characterized by FT-IR, ¹H-NMR spectroscopy, TGA and DSC. By UV irradiation, 4,5-dimethoxy-2-nitrobenzyl ester group decomposed satisfactorily to give alkali-developable polyimide, which was employed as a photolithographic system. Line-and-space patterns of 5 μm resolution with 10 μm thickness were achieved under an un-optimized lithographic condition. Due to its intrinsic photosensitivity, no photoinitiators or dissolution inhibitors were required. The PSPI reported in this work has many advantages such as easy and straightforward synthesis, high sensitivity, and minimized volume shrinkage due to fully-imidized polyimide.

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