

## Design, synthesis, and photosensitive performance of polymethacrylate-positive photoresist-bearing *o*-nitrobenzyl group

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**ABSTRACT:** Novel polymethacrylate-positive photoresist-bearing *o*-nitrobenzyl group was described herein. The matrix polymer (PCHIBNB) was synthesized by copolymerization of cyclohexyl methacrylate (CHMA), isobornyl methacrylate (IBMA), and *o*-nitrobenzyl methacrylate (NBMA) *via* reversible addition fragmentation chain transfer (RAFT) polymerization method. After UV irradiation, the *o*-nitrobenzyl groups of PCHIBNB were photocleaved and the resulting carboxyl groups were highly alkali-soluble, so that the matrix polymer could be etched by mild alkali solution with no requirements of photosensitizers or photoacid generators. PCHIBNB was characterized by Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy, and gel permeation chromatography (GPC). The photocleavable behaviors of PCHIBNB were determined by FTIR, <sup>1</sup>H-NMR, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) analysis. The resist formulated with this polymer and cast in tetrahydrofuran (THF) solution showed 10 μm × 10 μm square pattern using a mercury–xenon lamp in a contact printing mode and tetramethyl-ammonium hydroxide aqueous solution as a developer. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41733.

**KEYWORDS:** copolymers; optical properties; photochemistry; properties and characterization; resins

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### INTRODUCTION

Photoresist is a kind of etch-resistant thin-film material, and its solubility can change, when it is irradiated by many light sources, for example UV, excimer laser, electron beam, particle beam, and X-ray. As it is the basic chemical material for microfabrication in the field of optoelectronic information industry,<sup>1</sup> photoresist has been not only applied to the microfabrication of integrated circuits and semiconductor discrete devices, but also used for potential applications in many fields such as panel display, light-emitting diode (LED), magnetic head, precision sensors and so on.<sup>2</sup> Thus, the photoresist development has a great significance in the field of materials and information technology.

Photoresist is mainly composed of film-forming resin, photoacid generator, solvents, and a variety of trace additives. The film-forming resin is the main skeleton and basic material of photoresist. It also has a decisive impact on photoresist performances.<sup>3</sup> The regular photoresist resin systems include acrylic acid and acrylic esters,<sup>4–8</sup> polycyclic olefin polymer,<sup>9,10</sup> cyclic olefin, and maleic anhydride copolymer,<sup>11–13</sup> vinyl ether, and maleic anhydride copolymer,<sup>14,15</sup> polycyclic olefin ring-opening polymer,<sup>16,17</sup> multicopolymer.<sup>18</sup> Among them, acrylic esters system was widely used as it has a better resolution, sensitivity, and adsorptive property. However, traditionally it cannot be

etched alone unless photoacid generator and other diverse additives are used together, which inevitably raises the production cost and complicates the waste disposal process. Therefore, the objective of this work was to develop a simple photoresist system containing only a photosensitive polymer resin excluding photoacid generators.

*O*-Nitrobenzyl (*o*-NB) alcohol derivatives are commonly used as photolabile-protecting groups for carboxylic acid or amine groups in organic and polypeptide synthesis.<sup>19</sup> Having the easy accessibility and the quantitative cleavage upon UV irradiation, *o*-NB alcohol derivatives have attracted global interests in the field of material science.<sup>20</sup> Recently, *o*-NB alcohol derivatives have been applied in the production of photoresist materials.<sup>21</sup> The first example was reported by Neenan *et al.* using 2,6-dinitrobenzyl alcohol to prepare photoacid generators.<sup>22</sup> Another example adopted *o*-NB ether in the main chain of polyethers and suggested these materials for positive-type photoresists.<sup>23</sup> During the past decade, there were several excellent works demonstrating some polyimide and polymethacrylate systems, including *o*-NB group could be used as positive photoresist.<sup>24–29</sup> *O*-NB groups were used as photolabile-protecting groups for carboxyl acids UV irradiation, so that the photoresist resins could be etched alone without photoacid generators. These

polymer resins were synthesized by using polycondensation,<sup>24</sup> free radical polymerization<sup>25</sup>, and atom transfer radical polymerization (ATRP) methods.<sup>26–30</sup> Moreover, these photoresists were mainly applied in the fields of protein immobilization and incorporated very expensive monomers such as ethyleneglycol methacrylate<sup>26</sup> and fluoromethacrylate.<sup>30</sup> Thus, it motivated us to prepare some novel *o*-NB-containing photoresists by different polymerization method, adopting cheaper copolymerized monomers, and applying the conventional film patterning.

Inspired by all the above references, we designed a novel *o*-NB-containing polymethacrylate resin system with carbon-rich cyclic groups being incorporated as side groups in photoresist resin and used as acid-sensitive part so as to increase dry etch resistance. Meanwhile, the novel photoresist resin-bearing *o*-NB group was synthesized via reversible addition fragmentation chain transfer (RAFT) polymerization method, consisting of *o*-NB methacrylate (NBMA), isobornyl methacrylate (IBMA), and cyclohexyl methacrylate (CHMA). Its structure was characterized, and its lithography performance was studied.

## EXPERIMENTAL

### Materials

Methacryloyl chloride (MAC, 98%, Alfa Aesar) and *o*-NB alcohol (NBA, 98%, Alfa Aesar) were used as received without further purification. Isobornyl methacrylate (IBMA, 99%, Alfa Aesar) and cyclohexyl methacrylate (CHMA, Alfa Aesar, 99%) were passed through activated basic alumina columns before use.  $\alpha$ -Carboxyl propyl dithio benzoate (CPDB) was laboratory-made. Prior to use, azobisisobutyronitrile (AIBN, A.R.) was recrystallized from methanol, Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, A.R.) was distilled over calcium hydride. Tetrahydrofuran (THF) was refluxed over lithium aluminum hydride and purified by air distillation. Triethylamine (TEA, A.R.) was refluxed over calcium hydride for 12 h and distilled under vacuum. *N,N*-Dimethylformamide (DMF, A.R.) was distilled under vacuum and dried over 40 nm molecular sieves for 1 week. All the above-mentioned reagents and other solvents were purchased from Shanghai Chemical Reagent Company and used as received without further purification. Distilled water was used in all experiments.

### Synthesis

**Synthetic Route of PCHIBNB.** Methacryloyl chloride reacted with *o*-NB alcohol, and then photocleavable *o*-NB methacrylate was synthesized. PCHIBNB tetrapolymer-bearing *o*-NB group was synthesized via RAFT polymerization method, with CPDB as chain transfer agent, AIBN as initiator, IBMA, CHMA, and NBMA as monomers. The synthetic route was shown in Figure 1.

**Synthesis of *o*-NB Methacrylate (NBMA).** *o*-NB alcohol (2.56 g,  $1.67 \times 10^{-2}$  mol) and triethylamine (3.70 mL,  $2.56 \times 10^{-2}$  mol) were dissolved by dichloromethane (30.0 mL, 0.47 mol) in a 100 mL flask, and then, the flask was placed in an ice/water bath. The solution of methacryloyl chloride (2.20 mL,  $2.29 \times 10^{-2}$  mol) in dichloromethane (10.0 mL,  $1.57 \times 10^{-2}$  mol) was added dropwise into the flask from an additional funnel over a period of 10 min under nitrogen atmosphere. The reaction mixture was stirred for 24 h in ice/water bath.

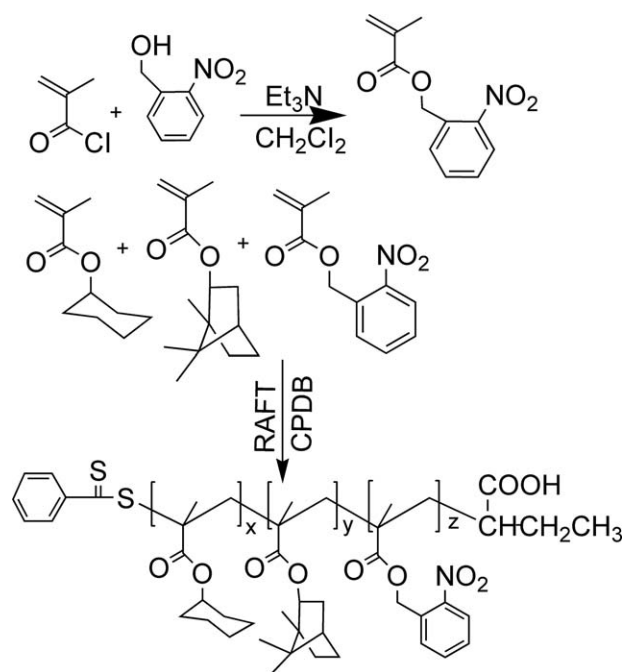


Figure 1. Synthetic route of PCHIBNB.

The mixture was sequentially washed with saturated aqueous sodium bicarbonate (NaHCO<sub>3</sub>) solution, water, and saturated aqueous sodium chloride (NaCl) solution. The organic phase was dried over anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) overnight, filtered, and then, the organic solvent was removed under vacuum. The yellow-brown crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1), affording a viscous yellow liquid (Yield : 95.6%).

**Synthesis of PCHIBNB.** The reaction solution containing CHMA (0.84 g,  $5 \times 10^{-3}$  mol), IBMA (1.10 g,  $5 \times 10^{-3}$  mol), NBMA (2.21 g,  $1.00 \times 10^{-2}$  mol), CPDB (0.032 g,  $1.30 \times 10^{-4}$  mol), AIBN (0.005 g,  $3.00 \times 10^{-5}$  mol) and DMF (1 mL,  $1.22 \times 10^{-3}$  mol) was bubbled with nitrogen for 30 min, then covered with a rubber stopper and sealed with poly(tetrafluoroethylene) adhesive tape. The mixture was stirred at 70°C for 12 h. The crude product was poured into a large amount of methanol and stirred. The precipitated white solid was filtered off, washed thoroughly with methanol, and dried in vacuum oven at 30°C for 12 h, and then, the white powder was obtained, named PCHIBNB. A series of PCHIBNB were synthesized from CHMA, IBMA, and NBMA through different reaction conditions, respectively.

**Irradiation of PCHIBNB.** PCHIBNB was dissolved in THF. After UV irradiation, *o*-NB photolabile groups of PCHIBNB were cleaved to pH-sensitive carboxylic groups. The irradiated polymer was dissolved in THF, precipitated in methanol, and then, PCHIBMA was obtained.

**Photoetching of PCHIBNB.** After a certain number of PCHIBNB was dissolved in THF (mass ratio = 1 : 10), the resist solution was prepared and filtered through a 0.22- $\mu$ m ultrafiltration membrane prior to coating. Silicon wafers were cleaned using a standard cleaning procedure: (1) NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O = 1 : 1 : 6

**Table I.** Polymerization Results of PCHIBNB Depending on Different Reaction Conditions

Sample	CHMA/IBOMA/ NBMA <sup>a</sup> mole ration	[M]/[C]/[I] <sup>b</sup> mole ration	Temperature (°C)	Mn (g/mol)	PDI	Yield (%)
P-1	1.0 : 1.0 : 0.5	200 : 1.0 : 0.25	70	6275	1.16	79
P-2	1.0 : 1.0 : 1.0	200 : 1.0 : 0.25	70	7027	1.22	76
P-3	1.0 : 1.0 : 1.5	200 : 1.0 : 0.25	70	7887	1.27	80
P-4	1.0 : 1.0 : 2.0	200 : 1.0 : 0.25	70	9032	1.31	87
P-5	1.0 : 1.0 : 2.5	200 : 1.0 : 0.25	70	11827	1.49	75
P-6	1.0 : 1.0 : 2.0	200 : 0.5 : 0.25	70	13590	1.53	85
P-7	1.0 : 1.0 : 2.0	200 : 0.7 : 0.25	70	11997	1.44	81
P-8	1.0 : 1.0 : 2.0	200 : 1.2 : 0.25	70	8083	1.30	75
P-9	1.0 : 1.0 : 2.0	200 : 1.5 : 0.25	70	6560	1.22	71
P-10	1.0 : 1.0 : 2.0	200 : 1.0 : 0.15	70	13981	1.25	77
P-11	1.0 : 1.0 : 2.0	200 : 1.0 : 0.20	70	11767	1.33	69
P-12	1.0 : 1.0 : 2.0	200 : 1.0 : 0.30	70	7832	1.46	70
P-13	1.0 : 1.0 : 2.0	200 : 1.0 : 0.35	70	6085	1.55	41
P-14	1.0 : 1.0 : 2.0	200 : 1.0 : 0.25	60	3322	1.26	69
P-15	1.0 : 1.0 : 2.0	200 : 1.0 : 0.25	65	6625	1.29	81
P-16	1.0 : 1.0 : 2.0	200 : 1.0 : 0.25	75	12204	1.45	86
P-17	1.0 : 1.0 : 2.0	200 : 1.0 : 0.25	80	15690	1.60	88

<sup>a</sup>Molar ratios of monomers were calculated based on initial concentrations before polymerization.

<sup>b</sup>[M] was the initial overall concentration of CHMA, IBOMA, and NBMA.

[C] was the initial concentration of chain transfer agent.

[I] was the initial concentration of initiator.

(70°C, 10 min); (2) rinse with ultrapure water (room temperature, 10 min); (3) rinse with ultra-pure acetone (10 min); (4) dried on a hot plate and activated (90°C). A resist film was prepared by spin coating of the resist solution onto a silicon wafer. Silicon wafer with resist film rotated at 500 rpm for 5 s and then rotated at 1500 rpm for 20 s. The resultant thin film was prebaked at 70°C for 60 s. Irradiation was carried out with a mercury–xenon lamp in a contact-printing mode. Photoetching was carried out on H94-25C photoetching machine at irradiation intensity of 0.5 mJ/(s cm<sup>2</sup>) for 120 s. The film was developed in tetramethyl ammonium hydroxide (TMAH, 2.38%) for 15 s, rinsed with deionized water, and then baked on a hot plate at 90°C for 60 s. Photoetching patterns were obtained with an optical microscope.

#### Measurements

FTIR spectra were carried out on a Nicolet Magna-IR 750 spectrometer at room temperature using KBr pellets. The spectra were obtained at a 4 cm<sup>-1</sup> resolution and recorded in the region of 4000~400 cm<sup>-1</sup>. <sup>1</sup>H-NMR spectra measurements were recorded on a Bruker AVANCE 300 NMR spectrometer, deuterated chloroform (CDCl<sub>3</sub>) as solvent, TMS as internal standard. UV-visible absorption spectra were measured on a SHIMADZU UV-2201 spectrometer (Japan) with the sample concentration of 0.04 g/L. The molecular weights and molecular weight polydispersity indices of polymer were estimated by Water 515–2410 GPC (Water, USA) at 45°C. Linear polystyrene standards were used for calibration and with tetrahydrofuran (THF) as the mobile phase. Thermogravimetric analysis (TGA) was recorded on SDT-Q600 (TA Instruments Ltd., USA). Sam-

ples (30–35 mg) were heated from room temperature to 800°C at a heating rate of 10°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments SDT-Q600 instrument from 0 to 250°C at a heating rate of 10°C min<sup>-1</sup> under a nitrogen purge. Irradiation experiments were carried out on H94-25C single-sided photoetching machine (Nanguang vacuum Science & Technology, Sichuan) in a contact printing mode at irradiation intensity of 0.5 mJ/(s cm<sup>2</sup>) for 120 s.

## RESULTS AND DISCUSSION

### Molecular Weight Distribution of PCHIBNB

As shown in Table I, RAFT polymerization results (i.e., molecular weights, molecular weight distributions and reaction yields of PCHIBNB) were markedly influenced by monomer molar ratios, initiator concentrations, chain transfer agent concentrations, and reaction temperatures. Among all these results, sample P-4 with a number-average molecular weight (9032 g/mol) and a sharp polydispersity index (1.31) obviously outweighs other polymer samples and is able to meet the requirements of photoresist resins. Thus, the detailed structural characterization and photolithographic performance tests of PCHIBNB were investigated based on sample P-4.

### Characterization of NBMA

The FTIR spectrum of NBMA was shown in Figure 2. The bands at 3110 cm<sup>-1</sup> and 895 cm<sup>-1</sup> were assigned to the stretching vibration absorption and the out-of-plane wagging vibration absorption of =C-H, respectively. The band at 1650 cm<sup>-1</sup> was assigned to the stretching vibration absorption of C=C.

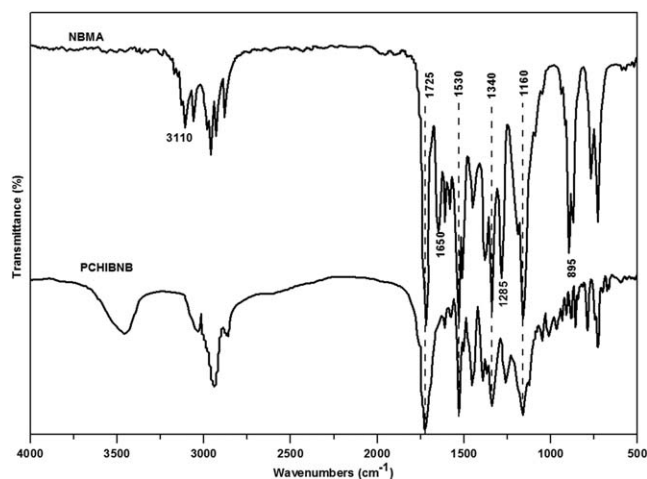


Figure 2. FTIR spectra of NBMA and PCHIBNB.

The characteristic absorption band at  $1725\text{ cm}^{-1}$  was attributed to C=O group of ester, and the bands at  $1285\text{ cm}^{-1}$  and  $1160\text{ cm}^{-1}$  were assigned to the stretching vibration absorption of C-O bond in ester. The bands at  $1530\text{ cm}^{-1}$  and  $1340\text{ cm}^{-1}$  were attributed to the stretching vibration absorption of N=O bond of  $-\text{NO}_2$  group, and the band at  $870\text{ cm}^{-1}$  was attributed to the stretching vibration absorption of C-N bond.

The  $^1\text{H-NMR}$  spectrum of NBMA was shown in Figure 3 (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.10 (d, 1H, ArH), 7.68–7.52 (m, 3H, ArH), 6.23, 5.88 (s, 2H,  $=\text{CH}_2$ ), 5.60 (s, 2H,  $-\text{O}-\text{CH}_2$ ), 2.00 (s, 3H,  $-\text{CH}_3$ ). According to the analyses of FTIR spectrum and  $^1\text{H-NMR}$  spectrum, it can be concluded that the reaction between *o*-NB alcohol and methacryloyl chloride took place as expected, and NBMA was synthesized successfully.

### Characterization of PCHIBNB

The FTIR spectrum of PCHIBNB was shown in Figure 2. The characteristic absorption bands of chief groups still existed in this copolymer, such as benzene ring ( $3036$ ,  $1610$ ,  $1576$ ,  $1505$ , and  $785\text{ cm}^{-1}$ ), C=O ( $1725\text{ cm}^{-1}$ ), and C-O bond ( $1260$  and  $1160\text{ cm}^{-1}$ ) of ester,  $-\text{NO}_2$  ( $1530$  and  $1340\text{ cm}^{-1}$ ), and C-N

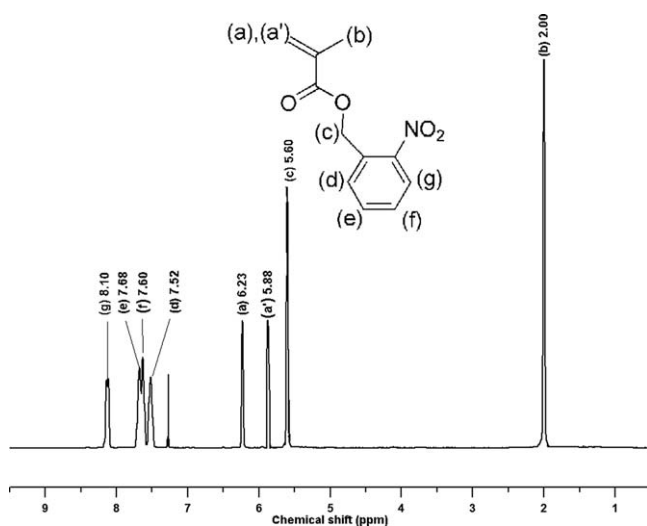


Figure 3.  $^1\text{H-NMR}$  spectrum of NBMA.

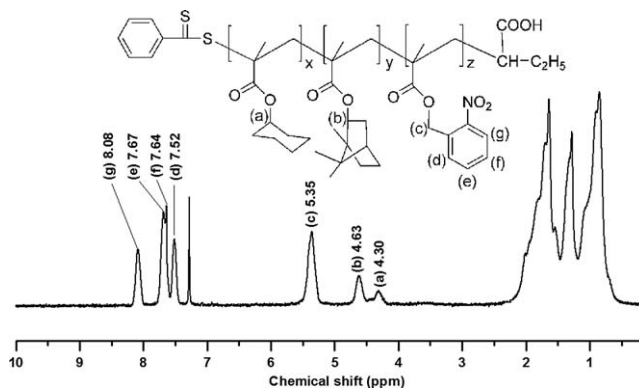


Figure 4.  $^1\text{H-NMR}$  spectrum of PCHIBNB.

bond ( $880\text{ cm}^{-1}$ ). However, the characteristic absorption bands of  $=\text{C-H}$  ( $3110$  and  $895\text{ cm}^{-1}$ ), and  $\text{C}=\text{C}$  ( $1650\text{ cm}^{-1}$ ) disappeared in PCHIBNB.

The  $^1\text{H-NMR}$  spectrum of PCHIBNB was shown in Figure 4 (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm). The aromatic protons of chemical shifts at 8.08, 7.67, 7.64, and 7.52 ppm were attributed to benzene ring. The aliphatic protons of chemical shift at 5.35 ppm were assigned to methylene of *o*-NB. The aliphatic protons of chemical shifts at 4.63 and 4.30 ppm were attributed to methine of isoborneonyl and cyclohexyl connecting to ester bond, respectively. Based on the integration ratios (2 : 0.8 : 0.7) of the above three peaks at  $\delta$  5.35, 4.63, and 4.30 ppm, we can roughly estimate the polymer composition with calculated molar percentages of *o*-NB (57.14%), isoborneonyl (22.86%), and cyclohexyl (20.00%) groups, although the designed molar ratio is 2 : 1 : 1. The chemical shifts ranging from 2.00 to 0.80 ppm were assigned to other protons. According to the analyses of FTIR spectrum and  $^1\text{H-NMR}$  spectrum, it can be concluded that the polyreaction of CHMA, IBMA, and NBMA took place as expected, and PCHIBNB was synthesized successfully.

### Characterization of PCHIBNB After UV Irradiation

After UV irradiation, PCHIBNB reacted as shown in Figure 5. To improve resolution, *o*-nitroso benzaldehyde was removed by precipitation. The exposure wave length is 365 nm UV light, and the irradiation intensity is  $0.5\text{ m J}/(\text{s cm}^2)$ . The FTIR spectra, UV-visible spectra, and  $^1\text{H-NMR}$  spectra of PCHIBNB before and after various UV exposure to 365 nm with different doses were shown in Figures 6, 7, and 8. According to Figure 6, after UV exposure to 365 nm with different doses, the bands at 3200 and  $1425\text{ cm}^{-1}$  were assigned to the stretching vibration absorption and the flexural vibration absorption of  $-\text{OH}$  in  $-\text{COOH}$ , respectively. Furthermore, the characteristic absorption bands of benzene ring ( $3036$ ,  $1610$ ,  $1576$ ,  $1505$ , and  $785\text{ cm}^{-1}$ ),  $-\text{NO}_2$  ( $1530$  and  $1340\text{ cm}^{-1}$ ), and C-N bond ( $880\text{ cm}^{-1}$ ) decreased remarkably and basically disappeared to the end. However, other characteristic absorption bands were hardly changed. Based on Figure 7, with the increase in UV exposure dose, the absorbances at 251, 283, and 338 nm decreased dramatically. It showed PCHIBNB had a good photosensitivity characteristic with high photospeed and excellent photobleaching effect, which benefited the performance of resist materials. According to Figure 8, with the increase in UV exposure dose,

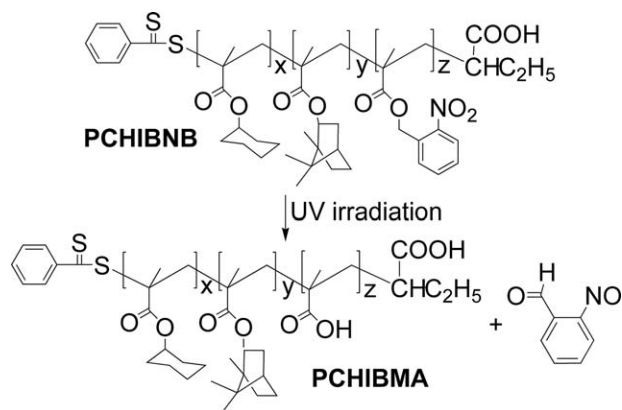


Figure 5. Photoreaction of PCHIBNB.

both aromatic protons of chemical shifts ( $\delta$  8.08–7.52 ppm) and aliphatic protons chemical shifts of  $-\text{CH}_2$  ( $\delta$  5.35 ppm) in *o*-NB reduced gradually and then basically disappeared to the end. The aliphatic protons of chemical shifts of  $-\text{CH}_2$  in isoborneonyl ( $\delta$  4.63 ppm) and in cyclohexyl ( $\delta$  4.30 ppm) connecting to ester bond had almost no distinct change.

It was the main reason that there were *o*-NB photolabile groups in side chains of PCHIBNB. After UV irradiation, *o*-NB ester bond in side chains of PCHIBNB was broken, *o*-nitroso benzaldehyde was removed, and *o*-NB photolabile protective groups were cleaved and turned to carboxyl groups. The increase in irradiation time could make *o*-NB ester bond break fully and turn to  $-\text{COOH}$ , and then, the amount of  $-\text{NO}_2$  reduced gradually. Thus, PCHIBNB was converted to PCHIBMA after UV irradiation.

#### Thermal Stability Analysis

In order to investigate the thermal properties of PCHIBNB, PCHIBNB was characterized by DSC during second heating scan at a heating rate of  $10^\circ\text{C min}^{-1}$  under a nitrogen atmosphere. As shown in Figure 9, the glass transition temperature ( $T_g$ ) of PCHIBNB was about  $144.5^\circ\text{C}$ , and it showed that PCHIBNB could meet the glass transition temperature basic requirements of photoresists.

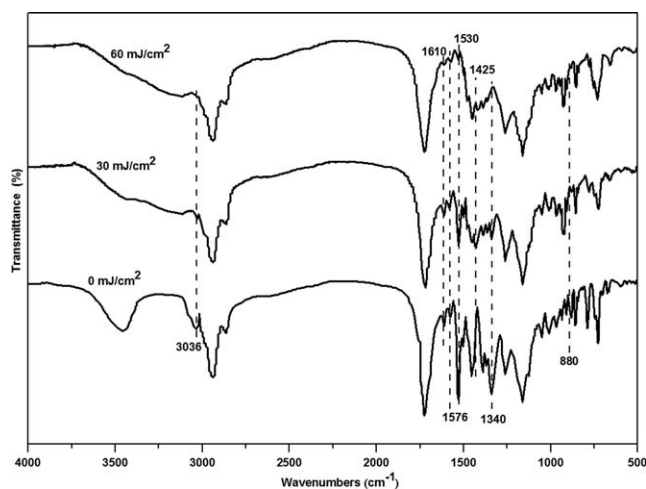


Figure 6. FTIR spectra of PCHIBNB before and after UV irradiation.

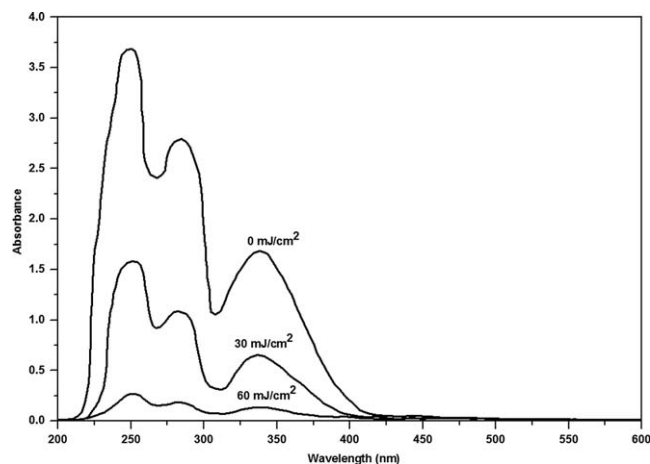


Figure 7. UV-visible spectra of PCHIBNB before and after UV irradiation.

The thermal properties of PCHIBNB before and after UV irradiation were investigated by TGA techniques. As shown in Figure 10, before UV irradiation, the temperatures of 5% and 10% weight loss ( $T_5$ ,  $T_{10}$ ) of PCHIBNB were about  $229^\circ\text{C}$  and  $252^\circ\text{C}$ , respectively. The TGA curve for PCHIBNB exhibited a smooth, stepwise manner, suggesting a three-stage pattern. The first-, second-, and the third-stage decompositions occurred at about  $200\sim 300^\circ\text{C}$ ,  $300\sim 360^\circ\text{C}$ , and  $360\sim 470^\circ\text{C}$ , respectively. The weight loss in the first stage was about 31.63% and close to the theory value 32.30% of *o*-nitroso benzaldehyde, and thus, it could be attributed to the rupture of *o*-NB ester bond in side chains of PCHIBNB, and then, *o*-nitroso benzaldehyde was removed. For the second-stage decomposition, 25.27% weight loss could be attributed to the degradation of both cyclohexyl and isoborneonyl segments in side chains of PCHIBNB, because the theory values of both cyclohexyl and isoborneonyl segments were about 9.93% and 16.39%, respectively. For the third-stage decomposition, 39.16% weight loss could be largely attributed to the main backbone of PCHIBNB. Compared with PCHIBNB,

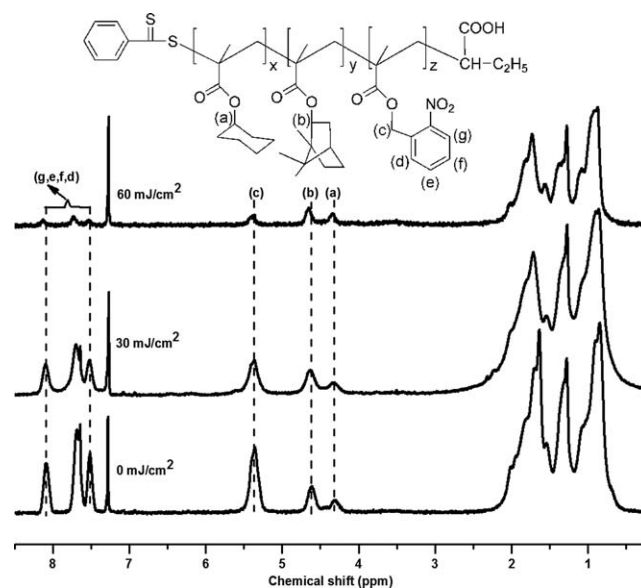


Figure 8.  $^1\text{H-NMR}$  spectra of PCHIBNB before and after UV irradiation.

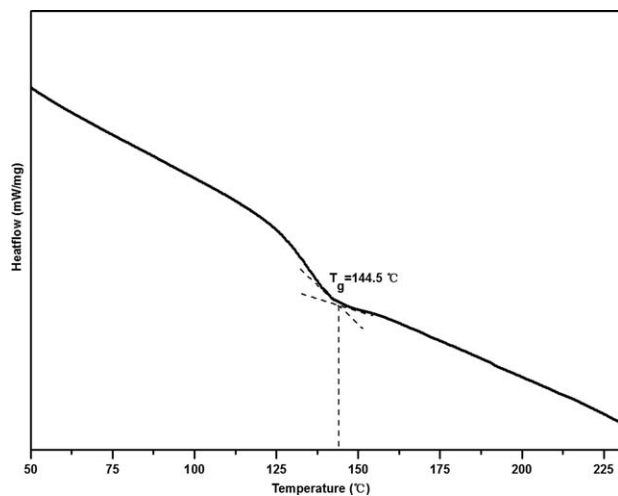


Figure 9. DSC curve of PCHIBNB.

the TGA curve for PCHIBMA showed a smooth two-stage pattern, the weight loss of PCHIBMA was about zero at temperatures below 250°C. The weight loss in the first stage was about 37.80% at temperatures ranging from 250°C to 360°C, which could be attributed to the degradation of both cyclohexyl and isoborneolyl segments in side chains of PCHIBMA. For the second stage at temperatures ranging from 360°C to 470°C, 57.24% weight loss was mainly attributed to the main backbone degradation of PCHIBMA. According to the above analysis, it could be concluded that PCHIBNB removed the *o*-nitroso benzaldehyde after UV irradiation and was converted to PCHIBMA as expected, and PCHIBMA had good thermal stability.

#### Photoetching Performance

After UV irradiation, PCHIBNB was converted to PCHIBMA, and then, there were many carboxyl groups in side chains, and therefore, it could be washed away easily and developed in TMAH with the concentration of 2.38% (w/w). The photolithographic pattern of PCHIBNB at a dose of 60 mJ/cm<sup>2</sup> was shown in Figure 11. The photolithographic patterns of PCHIBNB with different molar ratios of monomers at a dose of 60 mJ/cm<sup>2</sup> were shown in Figure 11. It could be seen that the molar ratio of monomers markedly influenced photolithographic perform-

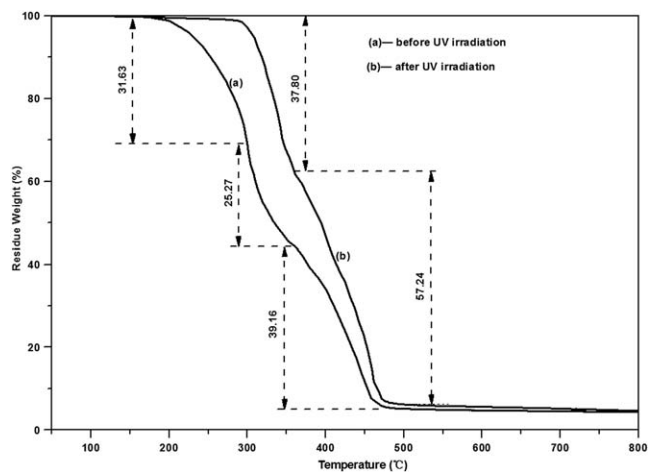


Figure 10. TGA curves of PCHIBNB before and after UV irradiation.

ance of PCHIBNB. In comparison, the photolithographic patterns of PCHIBNB (CHMA/IBMA/NBMA = 1.0 : 1.0 : 1.0 or 1.0 : 1.0 : 2.5) were obscure and lines were not very clear, while the photolithographic pattern of PCHIBNB (CHMA/IBMA/NBMA = 1.0 : 1.0 : 2.0) had excellent smoothness with no diffraction fringes or pinholes, and the line edges were very clear with high resolution. The irradiated areas of the resist film were dissolved in alkali liquor, and there was no swelling problem. The areas of the resist film without irradiation were not unaffected. It showed that PCHIBNB could be used as positive photoresist.

#### CONCLUSION

In conclusion, we designed and synthesized a new matrix polymer, PCHIBNB containing *O*-nitrobenzyl photolabile group and carbon-rich cyclic groups via RAFT polymerization method. As a positive photoresist, PCHIBNB resin system not only could be etched alone in alkali media without any other extra additives, such as photosensitizers and photoacid generators, but also could provide a clear photolithographic pattern. Compared with the other photoresist materials, PCHIBNB could be superior in serving the requirement of photoresists, with the advantages of reducing cost and alleviating environmental pollution.

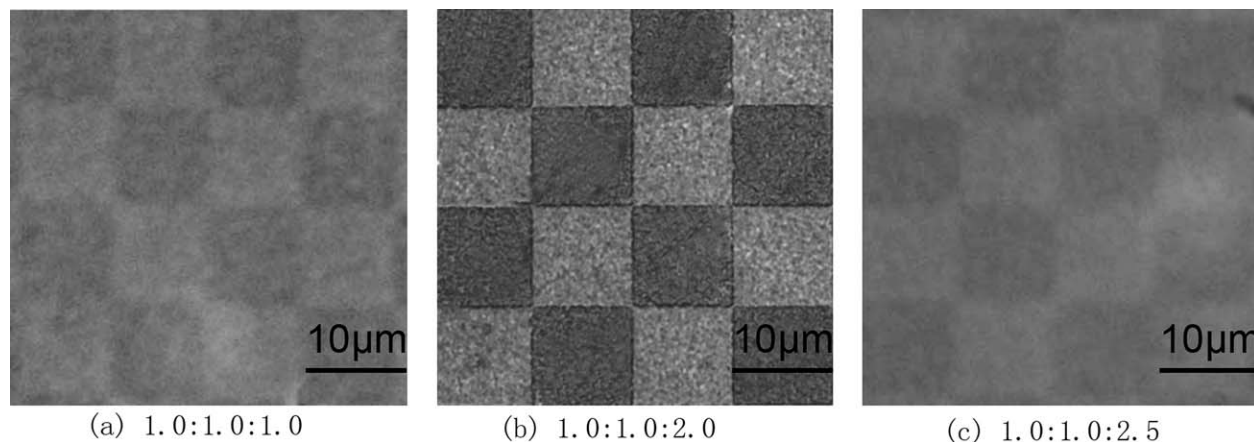


Figure 11. Photolithographic patterns of PCHIBNB with different molar ratios of three monomers.

We believe that PCHIBNB is a promising candidate to be the desirable photoresist main resin in the future.

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