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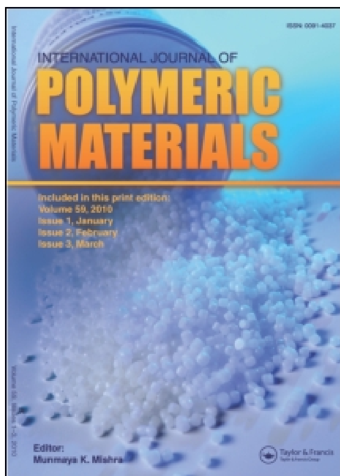

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Preparation of Substituted N-Methacryloxy Phthalimides for E-Beam Lithography

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Preparation of Substituted N-Methacryloxy Phthalimides for E-Beam Lithography

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Poly (methyl methacrylate) (PMMA) is a very good option for electron-beam resists, but suffers from poor radiation sensitivity and poor plasma etch resistance. These problems can be offset, at least in part, by functionalizing the PMMA with photolabile, plasma etch-resistance groups. Toward this end, a series of N-methacryloxy phthalimides with different substitutuents (methyl, nitro, tetrahydrogen and dichloro) were synthesized as possible useful radiation-sensitive resists. The work discussed here focuses on the cycloimido group, which can be easily attached to methacrylic acid to form a radiation-sensitive resist material for use in electron beam lithography. The labile N–O bond of the cycloimido group, upon exposure to radiation, cleaves and forms a radical on the main chain of the polymer, which leads to polymer degradation. Cursory evaluations showed that these new materials are deserving of further study.

Keywords: e-beam lithography, n-methacryloxy phthalimides, substitution

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INTRODUCTION

Moreau et al. [1] have synthesized an electron beam resist terpolymer using methyl methacrylate and methacrylic acid derivatives and found that it showed better sensitivity than PMMA. Backbone (radiation-induced) degradation (and, therefore sensitivity) in PMMA

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and its copolymers can be enhanced by replacing the α-methyl group with electronegative groups such as Cl and CN [2]. In order to overcome the problems of low etch resistance, poor processability, low resolution and poor sensitivity, workers have prepared PMMA-based polymers with various combinations of acrylic, alicyclic and aromatic systems. In spite of the in-depth research for development of electron beam resists, especially for extreme ultraviolet lithography, no clear solution has emerged.

A fundamental challenge in the development of PMMA resist materials for e-beam lithography (EBL) is the selection of side group. The pendant group must be strong enough to give sufficient thermal stability, etch resistance, and other mechanical properties compatible to microelectronic applications. At the same time they must be sensitive to electron beam exposure in order to make the polymer more soluble after exposure. As seen in the literature, recent workers continue to favor methyl methacrylate-based polymers (PMMA) as the promising e-beam resists [3]. But PMMA suffers from the fundamental drawback of poor sensitivity and poor plasma etching stability. This can be partially offset by functionalizing with stable pendant groups which are subsequently sensitive to radiation degradation.

We have developed several *N*-methacryloxy phthalimide monomers with various electron withdrawing and donating substituents (methyl, nitro, tetrahydro, and dichloro) to study the effect of these moieties on the sensitivity of the photoresists.

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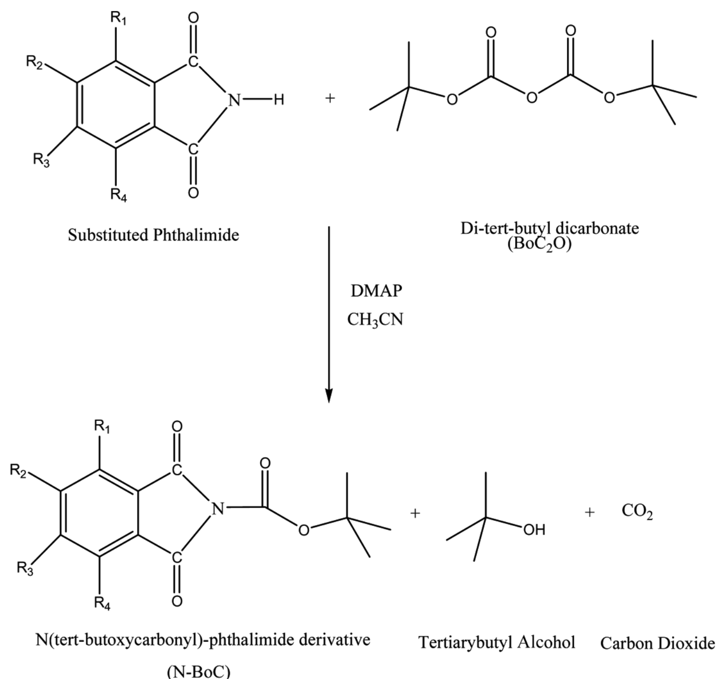
EXPERIMENTAL

Materials

All the substituted phthalimide compounds, 4-dimethylaminopyridine (DMAP), hydroxylamine solution, di-tertiarybutyl dicarbonate (BoC_2O), *N*-*N*-dicyclohexyl carbodiimide (DCC), tetrachloroethylene, trichloroethylene, methacrylic acid, azobis(isobutyronitrile) (AIBN) and methylmethacrylate (MMA) were purchased from Sigma-Aldrich. 4-Nitro-N-hydroxyphthalimide was purchased from TCI America. Reagent grade solvents were purified and dried by standard methods before being used in the reactions.

Monomer Synthesis

A one-pot synthetic procedure, developed by Einhorn et al. [4] was used to synthesize a series of substituted *N*-hydroxyphthalimides (Schemes 1, 2 and 3 and Table 1).



SCHEME 1 Synthesis of N-BoC derivatives from phthalimides.

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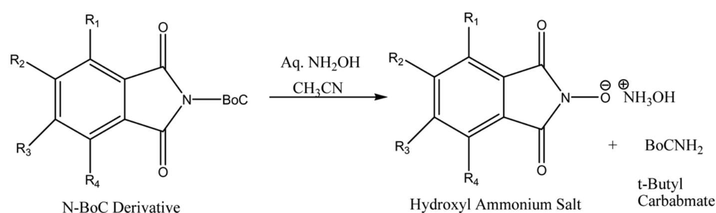
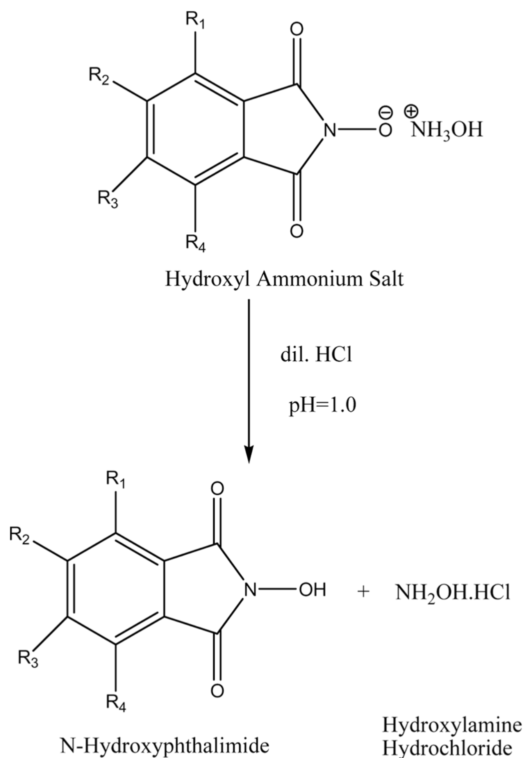
Acetonitrile (75 mL) was measured into a flask and phthalimide (22.1 g, 150 mmol) was added to it. After a homogeneous suspension was achieved, 4-dimethylaminopyridine (18.32 g, 150 mmol) was added and allowed to stir for two min. An appropriate quantity of di-tertiarybutyldicarbonate (1.5 eq, 150 mmol) was added to the suspension. A homogeneous solution of *N*-(tert-butoxycarbonyl)-phthalimide was obtained to which 150 mmol of aqueous hydroxyl amine solution (50 wt%) was added at room temperature. After the reaction was completed, 100 mL of ether was added to precipitate the hydroxyl



SCHEME 2 Synthesis of hydroxylammonium salt of phthalimides.



SCHEME 3 Synthesis of substituted *N*-hydroxyphthalimide.

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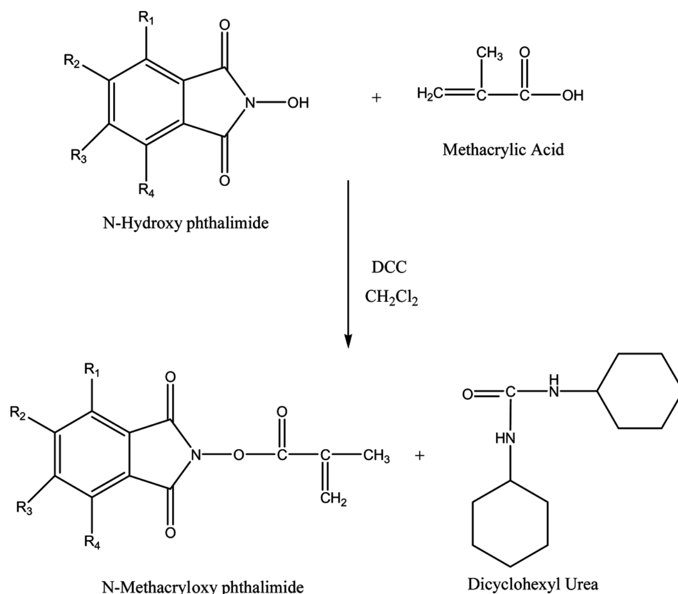
ammonium salt of phthalimide which was separated by vacuum filtration and washed twice with ether and dried.

The hydroxyl ammonium salt of phthalimide was homogeneously dispersed in water and acidified by adding 1.0 M hydrochloric acid until the pH of solution was 1.0. *N*-hydroxyphthalimide was separated by vacuum filtration, washed with water and dried under vacuum.

TABLE 1 Substituted *N*-Methacryloxy Phthalimides (NMPh)

Compound No.	Name	R_1	R_2	R_3	R_4
1	Poly(MMA-Chloro.NMPh)	H	Cl	Cl	H
2	Poly(MMA-Nitro.NMPh)	H	NO_2	H	H
3	Poly(MMA-NMPh)	H	H	H	H
4	Poly(MMA-Methyl.NMPh)	H	CH_3	H	H



SCHEME 4 Synthesis of substituted *N*-methacryloxy phthalimide.

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The Steglich esterfication reaction [5] was performed using *N*-hydroxyphthalimide and methacrylic acid to synthesize *N*-methacryloxy phthalimide compounds (Scheme 4). *N*-hydroxyphthalimide was suspended in dry methylene chloride [6]. Methacrylic acid was added dropwise to the suspension followed by the addition of *N,N*-dicyclohexyl carbodiimide (DCC). The urea derivative, dicyclohexyl urea, formed as a by-product was removed by vacuum filtration and the residue was washed with 20 mL of dry methylene chloride to remove any trapped product in the urea derivative. The filtrate was dried and was recrystallized from 95% ethanol to obtain purified *N*-methacryloxy phthalimide.

Monomers with other substituents were synthesized using similar procedures (Table 2) and the compounds were characterized using ^{1}H-NMR and IR spectroscopy. The characterization results were in agreement with the literature [6].

Polymer Synthesis

N-methacryloxy phthalimides were co-polymerized with methylmethacrylate (MMA) by free radical solution polymerization. Sufficient DMF was added to make a one molar solution [7]. AIBN

TABLE 2 Data for Synthesis of *N*-methacryloxy Phthalimide

Substitution	Starting Materials: *N*-hydroxy phthalimide (g)/(mmol)	Starting Materials: Methacrylic acid (g)	Starting Materials: DCC (mL)	Yield (g)/(%)	Melting point (°C)
4,5-Dichloro	8.45/36.4	3.13	7.51	7.49/65	117–118
4-Nitro	10.38/49.9	4.296	10.296	9.2/63	166–167
None	10.6/65	5.598	13.417	10.45/65	104–105
4-Methyl	9.3/52.5	4.25	10.84	6.3/46	135–136

was added as a free radical initiator. The solution was degassed and was maintained at 65°C for 20 h. The resulting solutions were precipitated into methanol. The product was filtered under vacuum, washed twice with water and dried under vacuum for 24 h (Table 3).

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Polymer Characterization

GPC was carried out for the polymers which were soluble in chloroform to determine the number average molecular weight (Mn) and weight average molecular weight (Mw). The molecular weight of the polymers was estimated based on calibration with polystyrene standards. The polymers were soluble in chloroform with the exception of homopolymers of 4-nitro-, 4-methyl- and unsubstituted *N*-methacryloxy phthalimides.

E-beam Lithography

A brief, cursory evaluation for susceptibility of the new copolymers to radiation lithography was conducted. Four polymer samples were dissolved (10% w/v) in 1,1,2,2-tetrachloroethylene. The resulting

TABLE 3 Copolymer Syntheses from Methyl Methacrylate and Substituted *N*-methacryloxy Phthalimide

Polymer name	MMA (g/mol%)	Substituted NMPH (g/mol%)	Ratio (mol%)	DMF (mL)	AIBN (mg)	Yield (g)/(%)
Poly(MMA-Chloro.NMPh)	2.5/24.97	2.5/9.05	76:24	33.3	54.68	4.4/88
Poly(MMA-Nitro.NMPh)	2.5/24.97	2.5/9.05	80:20	34.02	55.87	4.3/86
Poly(MMA-NMPh)	2.5/24.97	2.5/10.82	72:28	35.79	58.78	4.5/90
Poly (MMA-Methyl.NMPh)	2.5/24.97	2.5/10.2	79:21	35.17	57.76	4.6/92

solutions were filtered and spin-coated on 4 inch silicon wafers. The wafers were soft-baked at 110°C for 300 s.

All wafers were exposed to electron beam radiation using a 0.5 μm electron gun. A constant current of ~40 nanoamperes was applied over an array of patterns with line width varying from 0.06 μm to 1.5 μm and writing speed varying from 5000 μsec/mil to 1 μsec/mil.

The exposed resists were developed in a 70:30 mixture of isopropyl alcohol and trichloroethylene for 60 s followed by rinsing in isopropyl alcohol for 60 s. The exposed patterns were examined using an optical microscope.

RESULTS AND DISCUSSIONS

Monomer Synthesis

A series of *N*-methacryloxy phthalimides (Table 1) with different substituents were used as comonomers with MMA for polymer synthesis. A two-step procedure was used to synthesize all monomers, except 4-nitro-N-methacryloxy phthalimide, for which a single step esterification reaction (Scheme 4) was performed.

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N-(tert-butoxycarbonyl)-phthalimides

N-unsubstituted phthalimides cannot be oxidized to *N*-hydroxyimides; hence, they could not be used as precursors for synthesis of *N*-hydroxyphthalimides. Di-tert-butyl dicarbonate is a carbonate ester which reacts readily with the phthalimides in the presence of a catalyst such as DMAP, at room temperature, and forms the *N*-(tert-butoxycarbonyl) derivative (*N*-BoC derivative) of the compound (Scheme 1). The by-products of this reaction are t-butyl alcohol and CO_2, the former being soluble in the reaction medium. This reaction is fairly simple, highly efficient and gives good yields of *N*-BoC derivatives. The product was not isolated, but continued with the next step of synthesis.

After the starting material was converted to the *N*-BoC derivative of phthalimide (Scheme 1), addition of aqueous hydroxyl amine solution formed an orange precipitate which was the hydroxylammonium salt of *N*-hydroxyphthalimide (Scheme 2). Tert-butylcarbamate and tert-butyl alcohol, the by products of these reactions were completely soluble in the organic solution of the reaction medium.

N-Hydroxyphthalimides

This reaction medium of Scheme 2 was basic because of the presence of hydroxylammonium ion. At higher pH (>7), hydroxylammonium ion

dissociates into NH_2^+ and OH^- ions which explains the basic nature of the solution. On addition of hydrochloric acid, protons from HCl are transferred onto the hydroxylammonium ion and a salt of hydroxylamine hydrochloride, Cl^- NH_3^+ OH, was formed which was soluble in the aqueous medium. This increases the acidity of the solution and a sudden drop in pH was observed. Under highly acidic conditions, pH = 1.0, all hydroxylammonium ions are converted into the hydroxylamine hydrochloride favoring the formation of *N*-hydroxyphthalimides (Scheme 3). The product obtained was filtered under vacuum to separate the *N*-hydroxy compound from the aqueous solution of hydroxylamine hydrochloride. The residue was washed twice with water to ensure complete removal of the salt solution and dried to get sufficiently pure *N*-hydroxyphthalimides which were used in the final step of monomer synthesis.

The Steglich esterfication reaction was performed using N-hydroxyphthalimide and methacrylic acid to synthesize *N*-methacryloxy phthalimide compounds (Scheme 4). *N,N*-Dicyclohexyl carbodiimide (DCC) reacts with methacrylic acid to form an activated carboxylic acid, an *O*-acylisourea intermediate which reacts with N-hydroxyphthalimide and forms a stable dicyclohexyl urea and the ester. The urea derivative was removed by filtration under vacuum. Phthalimide was present in the homogeneous organic phase and was isolated by evaporating the filtrate under vacuum. The monomer was purified by recrystallization of the residue from 95% ethanol.

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Polymer Properties

The Tg of PMMA was 88°C and the Tg's of the copolymers ranged between 127 and 139°C (Table 4). Incorporation of NMPh monomers into the polymer increased the glass transition temperature as

TABLE 4 Properties of Copolymers of Methacrylate and Substituted *N*-methacryloxy Phthalimide

	Ratio				GPC		
Polymer name	MMA (mol%)	Substituted NMPH (mol%)	Tg (°C)	Tm (°C)	Mn	Mw	DPI
Poly(MMA-Chloro.NMPh)	76	24	138.81	291.56	23600	88600	3.75
Poly(MMA-Nitro.NMPh)	80	20	100.81	296.63	19100	41300	2.157
Poly(MMA-NMPh)	72	28	130.57	269.87	20700	53300	2.577
Poly(MMA-Methyl.NMPh)	79	21	127.28	292.34	18000	52900	2.940

expected. It was observed that there is only one glass transition temperature for each polymer; i.e. the polymerization did not result in a block copolymer. This implies that the monomer reactivity was likely random and that there was no phase separation. The π-stacking and ring structure of the aromatic groups increases the rigidity of the polymer. This reduces the flexibility of polymer chains and hence more energy has to be induced in order to overcome the interactions. The presence of a number of carbonyl groups also adds to the rigidity of the polymer. Because the bulky group is pendant and not a part of the polymer backbone, the rise in Tg was slight; however, it is important that Tg's of the polymers are high enough to withstand semiconductor processing.

The polymer degradation mechanism was expected to start either from the double-bonded chain ends or from the labile N–O bond on the pendant group of backbone. The decomposition temperature at maximum weight loss for the polymers ranged between 270 and 297°C. This sudden weight loss may be attributed to the formation of radicals on the backbone leading to the fragmentation of polymer. Small percentages of degradation were also observed in the TGA's. This might be from the loss of smaller molecules (or radicals) like CO_2, CO, OCH_3 or other pendant groups on the polymer backbone. Ultimate residues at 800°C of less than 10% indicate that most of the polymers expressed a very low char value, as expected for these aliphatic systems.

The polymers had molecular weights between 18000–24000 g/mol with polydispersity indeces (PDI) ranging from 2.1 to 3.0. (Table 4)

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E-beam Lithography Properties

Cursory electron beam lithography was done on silicon wafers coated with copolymers (20–28 mol% of NMPh) dissolved in chloroform on silicon wafers. These initial tests indicated that the presence of electronic donating or withdrawing groups on the chemical structure of the resist influenced the lithographic properties. The polymers with nitro and methyl substituents were observed to be the most promising materials as positive photoresists, indicating that further studies with these types of materials is warranted.

CONCLUSIONS

Four copolymers were synthesized from MMA and four differently substituted (nil, dichloro, methyl and nitro) N-methacryloxy phthalimides, the latter component designed to increase the sensitivity of

the polymers as e-beam resists due to the labile nature of the N–O bond under radiation. The copolymers contained from 72 to 80% MMA and were soluble and demonstrated Tg's from 127 to 139°C, considerably greater that PMMA. The copolymers were film formers and were coated on silicon wafers for cursory tests as resists. These results were sufficiently promising to warrant additional investigation.

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