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Synthesis of *N*-Substituted Maleimides and Poly(styrene-*co*-*N*-maleimide) Copolymers and Their Potential Application as Photoresists

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Poly(styrene-*co*-*N*-maleimide) copolymers bearing *tert*-butoxycarbonyl (*t*-BOC)-protected amine groups attached to side chains of varying lengths are synthesized via activators regenerated by electron transfer atom transfer radical polymerization (ARGET-ATRP) and investigated from the perspective of photoresist applications. The length of the alkyl substituents enables control of thermal properties as well as hydrophobicity, which are critically important for resist processing. Removal of the acid labile *t*-BOC group during deep-UV (DUV)exposure shifts solubility in the exposed areas and well-defined line space patterns of 1 µm are obtained for the selected copolymers. The correlation between glass transition temperature (T_g) and solubility contrast determines the lithographic performance where the copolymers with shorter alkyl chains exhibit promising results.

1. Introduction

Maleimide-based polymers have been widely used in engineering applications including coatings, 3D printing, transistor films, and photoresists due to their desirable properties such as high thermal stability and structural versatility.[1–5] One particularly important aspect of maleimides is the tendency of comonomer alternation during copolymerization with electron-rich (donor) monomers like styrene derivatives, which provide precise control of the sequence of copolymers. Maleimides comprise a versatile platform for functionalization of the copolymers, with various types of functional moieties or pendant chains.[6]

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Several studies have been conducted in recent decades to investigate the applicability of well-defined maleimide copolymers as photoresists. Utilization of acid labile protecting groups, which enable to adjust polarity upon deprotection of functional groups, as chemical amplifiers has attracted great attention The *t*-BOC group is widely used in chemically amplified resist systems and provides high sensitivity along with high-resolution.[7] Brunswold et al. synthesized thermally stable chemically amplified positive tone resists based on styrene-maleimide copolymers using *N*-(4-*t*-butyloxycarbonyloxyphenyl) maleimide.[8] Chatterjee et al. investigated *t*-BOC protected maleimide-styrene copolymer with onium salts as a positive deep-UV (DUV) resist combined with a series of additives to control the surface effects.[9] Schaedeli et al. examined the performance of copolymers of p-hydroxystyrenes and *N*-substituted maleimides as DUV resist as a function of the molecular weight and monomer ratio.[10]

Chiang et al. have demonstrated the use of various maleimide-based copolymers as DUV or near DUV photoresists.[4,11,12] For instance, a series of different *N*-(4-acetoxyphenyl) maleimide and different trimethylsilyl monomers were synthesized and copolymerized using free radical polymerization.[11] The resulting positive tone photoresists showed good thermal stability as well as good adhesion on a silicon substrate while patterns of 0.8 µm could be obtained. Another example has been shown by Shu et al.[13] Silicon containing poly(styrene-*co*-*N*-maleimide) copolymers were synthesized by radical polymerization and their structure, and thermal properties were studied for chemically amplified DUV photoresist applications.

In this study, copolymers of styrene and *N*-substituted maleimides with *t*-BOC protected amine groups attached to varying pendant chains were synthesized and investigated from the viewpoint of potential resist applications. The composition and molecular weights of the alkyl-based pendant chains were used to adjust solubility and thermal properties. DUV photolithography was demonstrated as a potential application of these copolymers. Films were patterned, through the removal of the acid labile *t*-BOC groups which induces change of polarity and creates a significant change in solubility of the copolymer in the exposed areas.

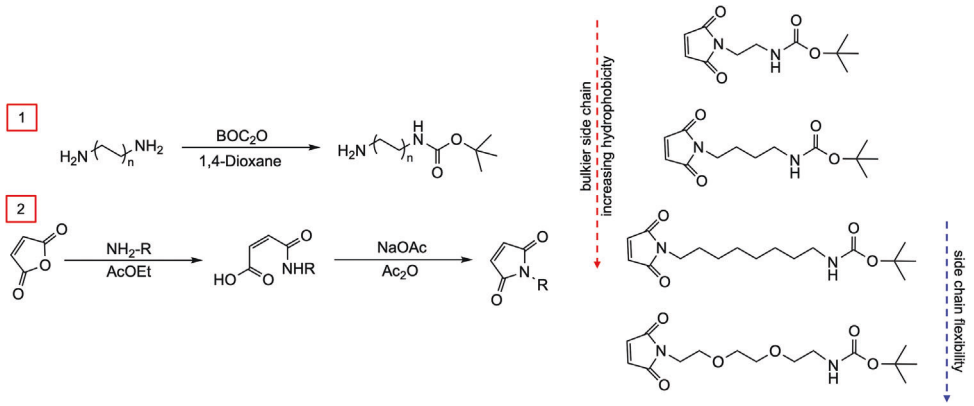

Figure 1. a) Synthesis of *N*-substituted maleimides via cyclization of maleamic acids b) *N*-substituted maleimides with varying pendant chains.

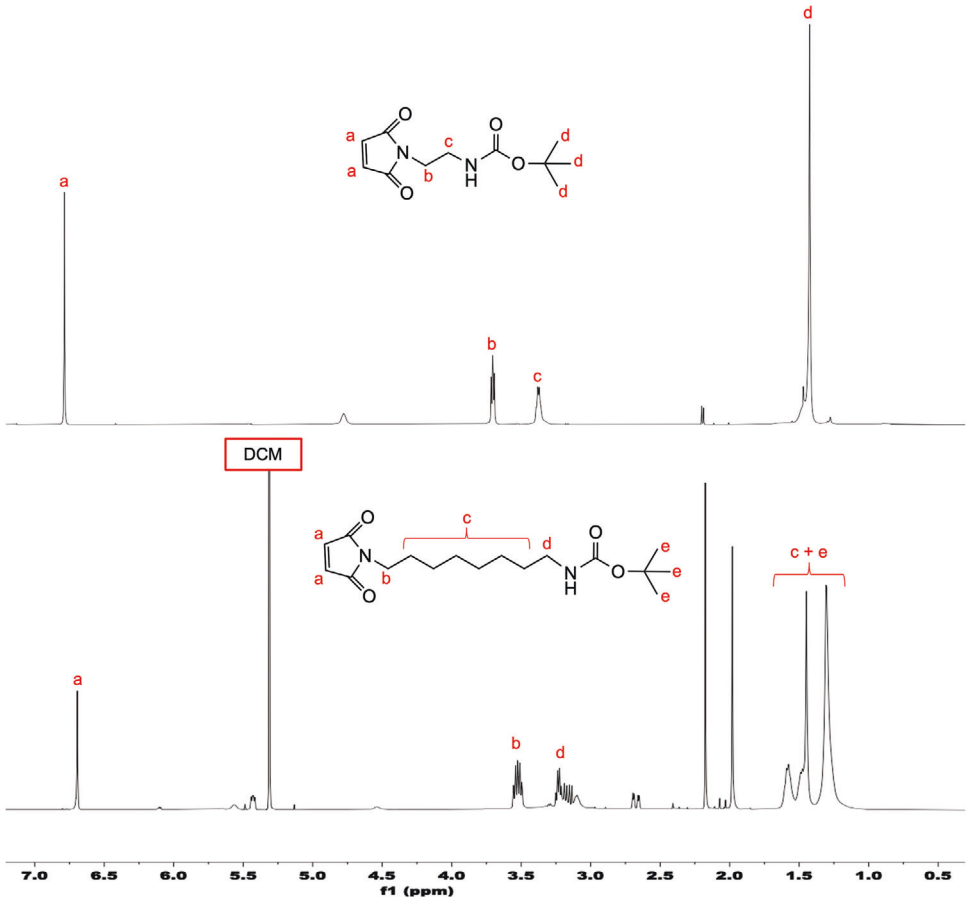

Figure 2. ^{1}H-NMR spectrum for *N*-(2-[(*t*-Boc) amino] ethyl maleimide and *N*-(8-[(*t*-Boc) amino] octyl maleimide recorded at RT in $CDCl_3$.

2. Results and Discussion

N-substituted maleimides with varying side chains have been synthesized according to a previously described procedure, through *t*-BOC protected alkane diamines and 2,2′-(ethylenedioxy)bis(ethylamine) (**Figure 1**).[14] *N*-substituted maleimides were obtained with good yields (80-95%) and representative proton nuclear magnetic resonance (^{1}H-NMR) spectra for *N*-(2-[(*t*-Boc) amino] ethyl maleimide and *N*-(8-[(*t*-Boc) amino] octyl maleimide are provided in (**Figure 2**).

Copolymers exhibited unimodal gel permeation chromatography (GPC) elugrams with narrow molecular weight distributions [Đ= 1.30–1.45]. The composition of copolymers was determined via ^{1}H NMR by comparing the integrations of aromatic protons of styrene (6.5–7.5 ppm) to the protons of *tert*-butyl groups (≈1.45 ppm) or methine and methylene groups of

Table 1. Characteristic of the copolymers.

Sample ID	M_n [a] [g mol^{-1}]	$Đ$	T_g [°C]	CA [°]
S1[b]	10 100	1.4	121.5	79.7 ± 0.4
S2[b]	10 200	1.3	92.7	87.4 ± 0.6
S3[b]	9300	1.4	63.1	90.9 ± 0.1
S4[c]	10 000	1.5	57.2	75.9 ± 0.1

[a] Based on PS standards; [b] 24 h; [c] 48 h.

maleimides. The characteristics of copolymers were summarized in **Table 1**. Representative NMR spectra for the selected copolymers are given in **Figure 3**a,b. Analyses showed that the copolymers are slightly rich in styrene, [St]: [MI] = 58:42, which might be a result of the bulky structure and electron-donating nature of substituted alkyl chains in the maleimide structure. The resulting products exhibited a pre-defined distribution of maleimide along the polymer backbone with precise localization of protected pendant chains which allowed the solubility change upon deprotection.

Thermal properties are critically important for the performance and processing of chemically amplified photoresists, where film processing requires pre- and postexposure baking steps mostly in a temperature range between 90 and 130 °C.[15] Differential scanning calorimetry (DSC) thermograms of the copolymers are given in (**Figure 4**). Glass transition temperatures (T_g) of Poly(styrene-*co*-*N*-maleimide) copolymers are strongly dependent on the side chain length and flexibility. The T_g of the copolymers with M_n around $10 \cdot 10^3$ g mol^{-1} varied between 121.5 and 57.2 °C, which decreased with increasing side chain length and flexibility, indicating higher mobility of the side chains with long alkyl substituents.

Photoresists have certain wettability requirements in applications to enhance surface adhesion and prevent dewetting. Thus, variation of wettability as a function of side chain structure was evaluated through water contact angle measurements. Increasing the length of the alkyl chain enhanced the hydrophobicity and the water contact angle (WCA) increased up to 90.9° which was found to be instead 75.9° for the oligo(ethylene glycol) containing copolymers (S4 in Table 1).

Copolymers with shorter pendant chains displayed higher T_g which offers advantages in terms of processing conditions and pattern integrity. Thus, copolymers with ethyl- and butyl-based side chains, S1 and S2, were selected for further evaluation. For DUV exposures, films were prepared by spin coating from the

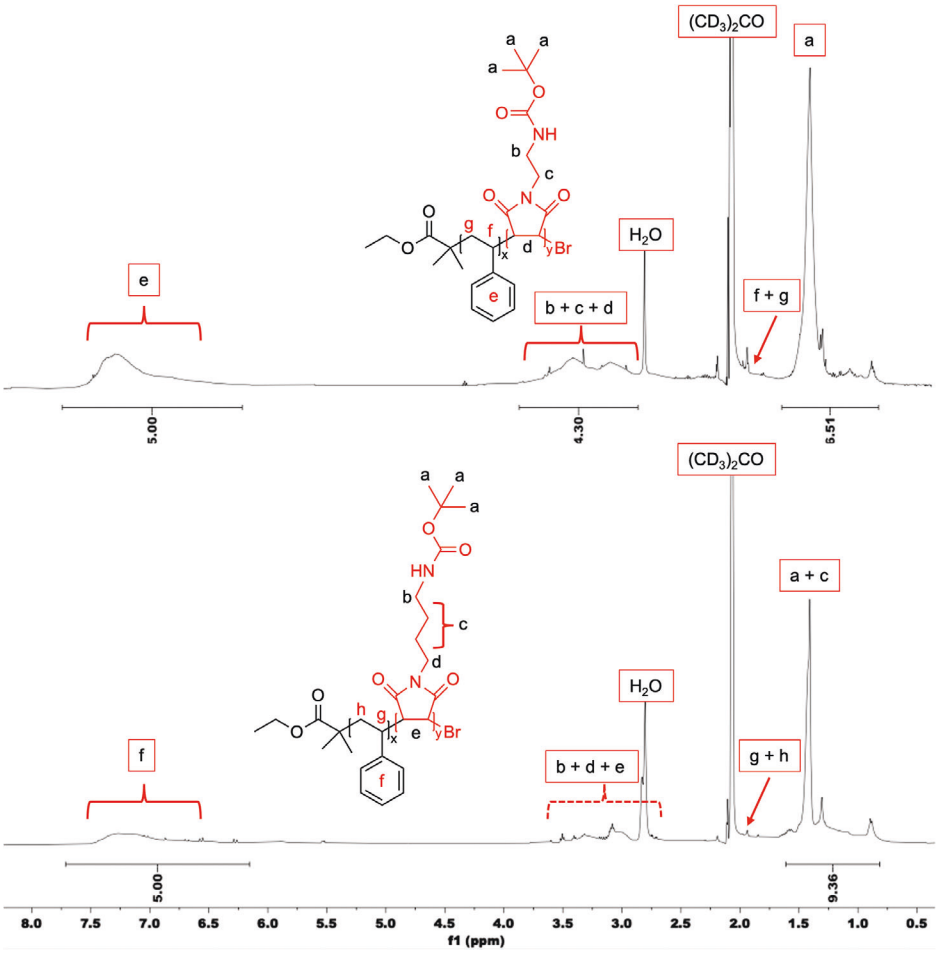

Figure 3. ^{1}H-NMR spectra of a purified Poly(styrene-*co*-*N*-(2-Boc-amino) ethyl maleimide) and Poly(styrene-*co*-*N*-(4-Boc-amino) butyl maleimide), recorded at RT in $(CD_3)_2CO$.

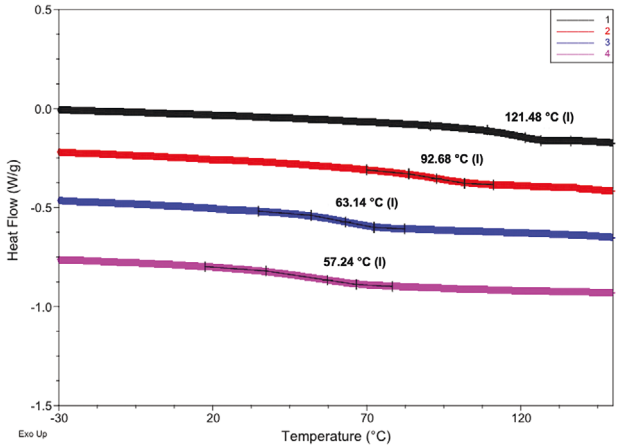

Figure 4. DSC thermogram of the copolymers.

solutions of copolymers in THF that contain 25 mg mL^{-1} copolymer and 20 wt.% triphenyl sulfonium triflate as photoacid generator. The films were postapply baked at 90 °C for 1 min to remove residual solvent. The film thicknesses were determined via ellipsometry as 50 and 100 nm for S1 and S2, respectively. Side chain deprotection induced a large change in solubility of the copolymers: the deprotected copolymers become soluble in aqueous solutions and the positive tone resists were developed in a mixture of 2-propanol and water (1:3 v/v) then the films were characterized using AFM (**Figure 5**). The line space pattern for the selected copolymers (S1 and S2 in Table 1) are shown in Figure 5b,c.

While both samples show promising results and defined line space pattern, it must be noted that S2 shows a better lithographical performance, i.e., fewer defects and roughness of the line pattern. This may be attributed to the enhanced hydrophobicity of S2 due to a longer alkyl side chain (C_4H_8) compared to that of S1 (C_2H_4), which leads to a limited change in solubility of the copolymer after exposure.

3. Conclusion

In summary, poly(styrene-*co*-*N*-maleimide) copolymers bearing *t*-BOC protected amine groups attached to the alkyl-based pendant chains were synthesized using ARGET-ATRP. Composition and length of the alkyl chains were used to adjust hydrophobicity and glass transition temperatures, which varied between 57.2 and 121.5 °C. Selected copolymers were utilized as chemically amplified DUV photoresists to demonstrate the potential application where 1μm line space patterns were obtained through the solubility changes in exposed areas Poly(styrene-*co*-*N*-maleimide) copolymers bearing *t*-BOC protected amine groups as attached to the alkyl based pendant chains displayed promising lithographic performance. Optimization of the side chain content, resist processing, and developing conditions will be the focus of future work.

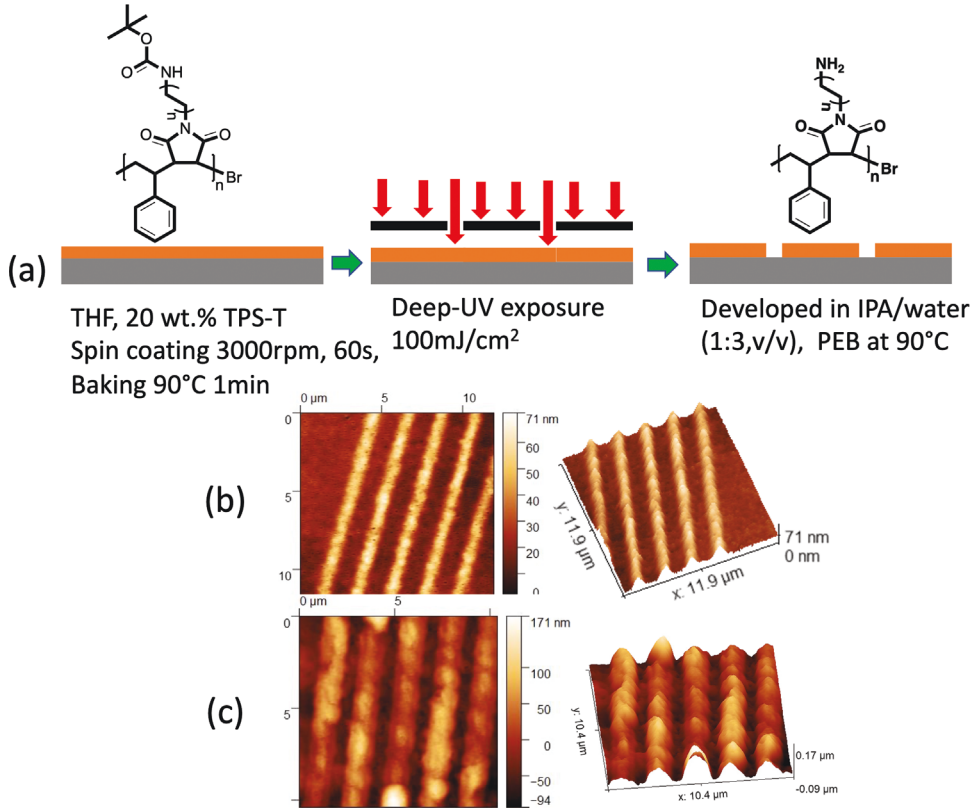

Figure 5. a) Schematic of DUV patterning of a positive tone poly(styrene-*co*-*N*-maleimide)copolymers, AFM images of 1 μm line space pattern b) S2, c) S1.

4. Experimental Section

Synthesis of N-Substituted Maleimides: *N*-substituted maleimides with varying side chains have been synthesized through *t*-BOC protected alkane diamines and 2,2′-(ethylenedioxy)bis(ethylamine). *N-t*-BOC monoprotected diamines with varying lengths of hydrocarbon/oligo ethylene glycol chains were introduced into the maleimides structure to adjust the solubility of the copolymers. First, side chains with amine groups were prepared by reacting diamines with di-tert-butyl dicarbonate in dioxane (6:1 molar excess of alkane diamine to di-tert-butyl dicarbonate). For the synthesis of maleimides, equimolar amounts of maleic anhydride and *N-t*-BOC monoprotected diamines were reacted in ethyl acetate, except for 1,8-diaminooctane where toluene was used due to the solubility limitation, which resulted in maleamic acid intermediates. Maleamic acid intermediates were subsequently dehydrated into the corresponding cyclic maleimides by heating (55 °C) in the presence of anhydrous sodium acetate, and the excess amount of acetic anhydride. Cyclization proceeded smoothly with 0.3 molar equivalent of sodium acetate and 5.5 molar equivalent of acetic anhydride, giving good yields (80–95 %) of the desired maleimides.

Synthesis of Poly(Styrene-Co-N-Maleimide) Copolymers: Poly(styrene-*co*-*N*-maleimide) copolymers were synthesized via ARGET ATRP to explore the effects of side chain length and composition on solubility and thermal behavior. Polymerization conditions were optimized through preliminary studies and were carried out with L-ascorbic acid as the reducing agent under the following conditions [MI]/[St]/[EBiB]/[$CuBr_2$]/[Me_6TREN]/ [L-ascorbic acid] = 250/250/1/0.05/0.5/1.5 in DMF at 110 °C. The polymers were precipitated in DIW and washed with methanol then dried under vacuum for 12 h. Copolymers were analyzed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC, based on PS standards) to determine the composition and molecular weight.

GPC Analyses: Molecular weight (M_n) and dispersity (Đ) of the polymers were measured with Agilent 1200 gel permeation chromatography (GPC) instrument using three PSS SDV columns (with molecular weight ranges of 1000–10 000, 1000–1 210 000 g mol^{-1}) with a refractive index detector at 35 °C. THF was used as eluent with a flow rate of 1.0 mL min^{-1}, based on PS standards.

^{1}H NMR spectra of *N*-substituted maleimides and polymers were recorded on a Varian Inova 500 spectrometer operating at 500 MHz at room temperature.

AFM Analyses: The microstructured films were characterized using Oxford Instruments Cypher ES atomic force microscope (AFM) equipped with an environmental scanner in tapping mode. Silicon tips (Oxford Instruments) with a resonance frequency of 300 kHz and 26 N/m spring constant were used.

CA Measurements: WCA were performed using an Attension Theta Lite goniometer using the sessile drop method, data were collected for a 10 s period within 60 s. The measurement process was repeated four times and average values are reported.

DSC Analyses: Thermal analyses of the copolymers were conducted by a predetermined method, through the Differential Scanning Calorimetry (DSC, TA instruments Q2000 series). Two cycles of heating/cooling were applied to eliminate the thermal history of the samples. The heating ramp was arranged from −50 to 120 °C for the first cycle and from −50 to 250 °C for the second one with a rate of 10 °C min^{-1}. Reported data were evaluated from second heating cycles.

Deep-UV patterning: The polymers were dissolved in THF (20 mg mL^{-1}) and 20wt.% Triphenylsulfornium-triflate (TPS-T) was added in relation to the mass of polymer. The solution was sonicated for 5 min and filtered using a 0.22 µm PTFE syringe filter. The resists were spin-coated on a 4 inch wafer (3000 rpm, 60 s) and preexposure baked for 60 s at 90 °C. The film thickness was determined using a Woollam RC2 Spectroscopic Ellipsometer. DUV exposures were carried out using an ASML PAS 5500/300C DUV Wafer Stepper. The resists were developed in a mixture of 2-propyl alcohol/water (1:3, v/v) for 30 s.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

alternating copolymers, ARGET-ATRP, DUV photolithography

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