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Novel High-Index Resists for 193 nm Immersion Lithography and Beyond

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ABSTRACT

A preliminary Quantitative Structure Property Relationship (QSPR) model for predicting the refractive index of small molecules and polymers at 193 nm is presented. Although at this stage the model is only semiquantitative we have found it useful for screening databases of commercially-available compounds for high refractive index targets to include in our program of synthesis of high refractive index resist polymers. These resists are targeted for use in 2nd and 3rd generation 193 nm immersion lithography. Using this methodology a range of targets were identified and synthesized via free radical polymerization. Novel resist polymers were also synthesized via Michael addition polymerization. Preliminary dose to clear experiments identified a number of promising candidates for incorporation into high refractive index resist materials. Furthermore, we have demonstrated imaging of a high index resist using water-based 193 nm immersion lithography.

Keywords: High refractive index polymers, QSPR, Imaging, 193 nm Immersion Lithography

1. INTRODUCTION

193 nm immersion lithography involves a photolithography resolution enhancement technique that replaces the air gap between the final lens element and the photoresist coated silicon wafer, with a fluid that has a refractive index greater than air. The resolution enhancement compared to dry lithography is directly related to the refractive index of the fluid used. Current 193 immersion lithography tools use ultra pure water for the fluid, and feature sizes of the order of 45 nanometers have been reported. Advances in immersion fluid, resist and lens design are required to extend 193 nm immersion lithography to the 32 nm node or below. An additional advantage of an increased RI of the fluid is an increase in the depth of focus for the process. Increases in the refractive index (RI) of the immersion fluid (the optical element currently with the lowest RI) are being sought by a number of groups,^[1-4] with the aim of increasing the numerical aperture of a system, in turn leading to a reduction of the possible feature size. Water, the first generation immersion fluid has an RI of 1.44 and the targets for the RI of the 2nd and 3rd generation fluids are 1.65 and 1.8 respectively.

Significant improvements to immersion lithography are also expected when the RI of the resist is increased beyond the current average value of 1.65. Specifically, theoretical calculations have shown that an increase in the RI of the polymeric resist, to a value of around 1.9-2.0, will result in an increase in the exposure latitude, contrast and MEEF.^[5] We have recently reported the design and synthesis of novel polymers with increased RI for use in future immersion resist formulations.^[6, 7] An essential part of the discovery process is the use of quantitative structure-property relationships (QSPR) models, developed by us, to predict the refractive index of small molecules and polymers. Initially we used a model consisting of a set of nine descriptors, which were determined to describe the RI of a large dataset of molecules at 589 nm. The Cauchy equation was then used to predict the RI at 193 nm. This methodology was reasonably successful for non-absorbing compounds, but the relationship was poor for compounds with absorption bands near 193 nm. In this paper we describe a preliminary QSPR model that predicts RI at 193 nm and its use in our high refractive resist synthetic program.

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2. MATERIALS AND METHODS

2.1 Materials

All chemicals were obtained from Sigma Aldrich, and were generally used as received without further purification.

2.2 QSPR Modeling

The geometries of the model compounds were first optimized with the semi-empirical AM1 method, using the AMPAC software package and then descriptors were calculated using the CODESSA software package. The heuristic method was applied to find the best one-parameter correlations. Using these one parameter correlations the most significant descriptors were determined using multi-linear regression to find the best predictive model.

2.3 Monomer Synthesis

Typical Synthesis of Methacrylate, Thiomethacrylate and Methacrylamide Monomers (M1-M5), using M5 as an example

In a round bottle flask, 2-thiophenemethanol (1 eq) and triethylamine (1.05 eq) were dissolved in dichloromethane. The reaction vessel was cooled to 0 °C and purged with dry nitrogen and then methacryloyl chloride (1.05 eq) was added drop-wise. The reaction was allowed to warm to 25 °C and stirred for 16 hours. The reaction mixture was filtered, diethyl ether was added to the organic layer, which was then washed with 3% HCl_(aq.), saturated NaHCO₃, and distilled water three times, respectively. The compound was concentrated and characterized by ¹H NMR (CDCl₃): 7.30 (CH), 7.10 (CH), 6.98 (CH), 6.14 (s, CH), 5.57 (q, CH), 5.30 (CH₂), 1.95 (CH₃).

Synthesis of Dithiol 1 for use in Michael Addition Polymerization

The trisulphide was synthesized using a previously described method.^[7] Reduction of the trisulphide was achieved using NaBH₄ in ethanol^[8] (see Fig. 3) to afford dithiol **1** in good yield.

2.4 Polymer Synthesis

Typical homopolymerization of M1-M5 using polymerization of M5 to yield P5 as an example

M5, tetrahydrofuran (50%wt), and 1mol % azobisisobutyronitrile were added to a glass tube and were subjected to three freeze-thaw vacuum degassing cycles and were then flame sealed under high vacuum. The polymerization mixture was heated to 60 °C for 24 hrs. Molecular weight was characterized by gel permeation chromatography.

Copolymerization of M1-M5 with 1-methyladamantyl methacrylate (MAdMa), using M5 as an example

M5 (50 mol%), MAdMa (50 mol%), tetrahydrofuran (50%wt), and 1mol % azobisisobutyronitrile were added to a glass tube and were subjected to three freeze-thaw vacuum degassing cycles and were then flame sealed under high vacuum. The polymerization mixture was heated to 60 °C for 24 hrs. Molecular weight was characterized by gel permeation chromatography.

Michael Addition Polymerization of CP3

Reaction of divinyl sulfone with norbornene dithiol monomer **1** at room temperature in the presence of 0.5 equivalents of TEA for 24 hours afforded copolymer CP3 (M_n 17,300; PDI 1.7) as a semi-transparent solid. Since the desired molecular weight was less than 10 k Da modified conditions were employed to reduce the molecular weight closer to this target range. Reaction at room temperature for 4.5 hours gave a lower molecular weight polymer (M_n 3905; M_w 5024; PDI 1.3).

2.5 Polymer Characterization

NMR: ¹H and ¹³C NMR were performed on a Bruker 500 MHz or 300 MHz spectrometer with a TXI probe. For ¹H NMR at least 32 scans were acquired, while for ¹³C NMR at least 256 scans were acquired.

GPC measurements were performed using a Waters 2695 separation module with three linear (2 x Styragel followed by 1 x Ultrastyrigel) columns in series. Samples (1 mg ml⁻¹ in THF) were eluted with THF at a rate of 1 ml min⁻¹ at 30 °C and detected using a Waters 410 differential refractometer. The molecular weight as a function of retention volume was calibrated using low polydispersity (PDI ~ 1.03) polystyrene standards and the molecular weights are reported with respect to polystyrene.

Refractive index measurements were determined from spectroscopic ellipsometric measurements made on a J.A. Woolam M-2000 variable angle spectroscopic ellipsometer or a JA Woollam VUV spectroscopic ellipsometer.

3. RESULTS AND DISCUSSION

3.1 Identification of Targets with High Refractive Index at 193 nm

The basis of our strategy has been to develop quantitative models that are able to predict the refractive index of small molecules and polymers, and then utilize these models to guide us in our synthetic efforts. Initially, we prepared a QSPR model that was able to predict the refractive index of small molecules and polymers at 589 nm and we then used the Cauchy equation to estimate the refractive index at 193 nm.^[7] This was successful to some extent for non-absorbing compounds, however, the relationship was not as robust when materials had absorption bands near 193 nm. Hence, we have measured the refractive index of 64 small molecules at 193 nm and formulated a QSPR model. From this set of molecules a correlation coefficient of 0.87 has been obtained (see Fig. 1). At this stage the model is not mature enough to allow quantitative predictions, however, it is still useful for guiding our synthetic efforts.

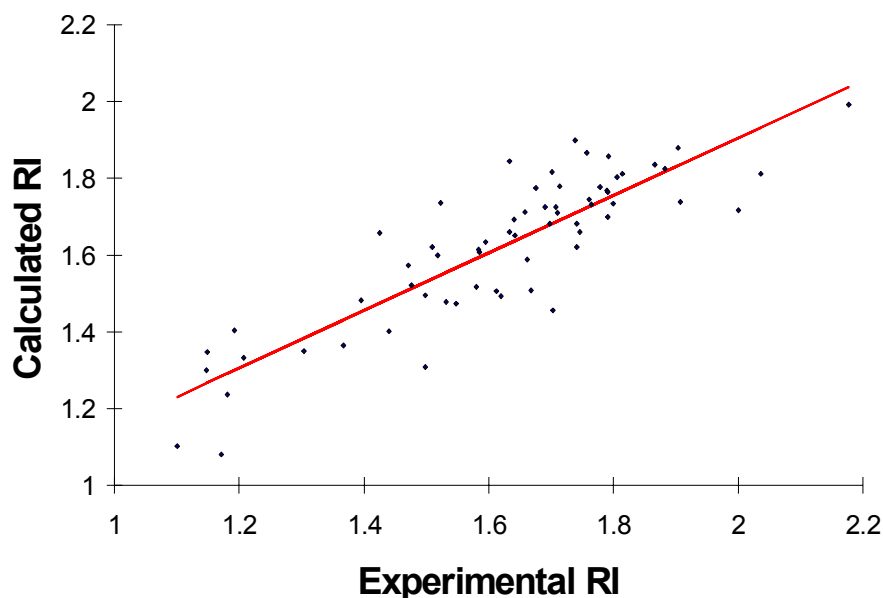
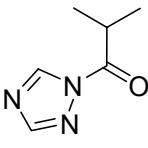
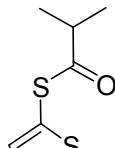
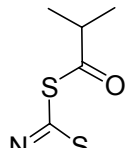
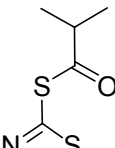
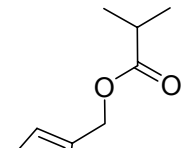


Fig. 1. Preliminary QSPR model for the prediction of the RI of small molecules and polymers at 193 nm.

Table 1. Predicted RI values for 193 and 589 nm for a series of target model compounds identified by our QSPR models at 589 and 193 nm.

Structures	T1	T2	T3	T4	T5
					
Predicted $n_{589\text{ nm}}$	1.70	1.69	1.68	1.71	1.62
Predicted $n_{193\text{ nm}}$	1.96	1.90	1.88	1.90	1.81

The RI targets for resists to be used in 2nd and 3rd generation immersion lithography that have been suggested by Conley *et al.*^[5] are in the order of 1.9-2.0. We have utilized this preliminary model to screen chemical databases, such as the

Aldrich catalogue, for structures that have high RI at 193 nm. The structures from this first-pass screening were ranked based on RI and on functional groups that are compatible with easily assessable synthetic methods and that are also compatible with free radical polymerization. Polymer-based analogues of these structures were reassessed with the model to generate a refined list. Table 1 shows some examples (T1-T5) of structures that were predicted to have high refractive indices at 589 nm as well as at 193 nm based on our QSPR. It should be noted that T5 was still chosen even though it has a predicted RI at 193 nm of 1.81 due to the uncertainty of estimation of our current QSPR model.

Target structures T1, T3 and T4 contain tertiary nitrogen atoms, which have the potential to be basic and thus may detrimentally affect imaging performance of a resist by quenching any photo acid that forms during irradiation and post exposure bake steps. However, a survey of the values of pK_b of some tertiary nitrogen compounds that have been reported in the literature indicates that a wide range of values can be obtained for different structures (see Table 1). Hence, the nitrogen containing targets have remained on the list of synthesis candidates, because their basicity is thus far unknown.

Table 2. Structure dependence of N-containing compounds and their basicity.

Structure	TBAH (polar medium)	TBAH (non-polar medium)	Piperidines	Pyridine	Triazoles
pK_b	3.1	5.8	10 - 11	8.75	1.2

3.2 Synthesis of Monomers (M1-M5) and Homopolymers (P1-P5) for Model Validation and Characterization of Optical Properties

Commercially-available precursors for targets T1 – T5 were available as amines, thiols or alcohols. These compounds were reacted with methacryloyl chloride in the presence of a base to yield the corresponding methacrylamide, thiomethacrylates and methacrylate (See Fig. 2)

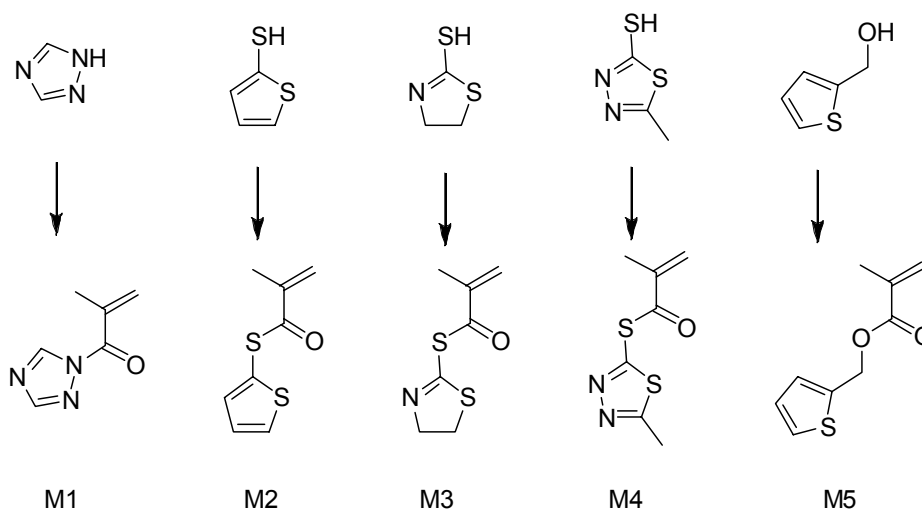


Fig. 2. Precursors were reacted with methacryloyl chloride to generate corresponding monomers

Monomers M1-M5 were polymerized by standard free radical polymerization using AIBN as an initiator.

Table 3 shows the structures of the polymers synthesized as well as the predicted RI values at 193 nm. Of the polymers synthesized, it was found that only P3 – P5 were able to generate good quality films by spin casting from a solution of PGMEA. The RI values, as determined by ellipsometry, for P3-P5 are also shown in Table 3. It was found that the

current iteration of the 193 nm QSPR model underestimates the RI of the polymers by approximately 0.1 units. Nonetheless, for this series of polymers the model has been successful in identifying high refractive index candidates.

Table 3. Structures of homopolymers synthesized in this study along with their predicted and experimentally determined RIs at 193 nm.

Structures	P1	P2	P3	P4	P5
Predicted $n_{193 \text{ nm}}$	1.96	1.90	1.88	1.9	1.81
Experimental $n_{193 \text{ nm}}$	n/a	n/a	2.01	1.98	1.92

3.3 Synthesis of Resist Copolymers and Optical Characterization

3.3.1 Synthesis of CP1 and CP2

CP1 and CP2 were synthesized via free radical polymerization of M4 and M5 with MAdMa, using AIBN as a thermal free radical initiator. A 1:1 mole ratio of sulfur-containing monomer in relation to the MAdMa was used. These polymers were spin cast onto silicon wafers from a 1% solution in PGMEA. CP1 was found to have a refractive index of 1.7 and an absorbance of $5.22 \mu\text{m}^{-1}$, while CP2 was found to have a refractive index of 1.76 and an absorbance of $5.22 \mu\text{m}^{-1}$. These results indicate that a reduction in the refractive index of the copolymers relative to the homopolymers has occurred, which is expected from Van Krevelen's group contribution theory. The absorbance values of CP1 and CP2 are slightly higher than what is probably acceptable for use as 193 nm resists. However, in subsequent generations of these polymers the proportion of the high refractive index copolymer can be adjusted such that an acceptable absorbance value is obtained. We are also in the process of identifying further high RI polymer components that are less absorbing.

Table 4. List of resist copolymers prepared as part of this study, as well as some of their optical, physical and imaging properties.

Structures	CP1	CP2	CP3
$n_{193 \text{ nm}}$	1.70	1.76	1.80
Abs (μm^{-1})	5.22	5.22	7.2
T_g	106	166	140
M_w	10.8 k	68k	5k
E_0	25 mJ/cm^2	5.5 mJ/cm^2	3 mJ/cm^2

3.3.2 Synthesis of CP3 via Michael addition polymerization

Free radical polymerization has a limit as to how much sulfur can be easily incorporated into a polymer structure. Previously, we have demonstrated that sulfur can easily be incorporated into the backbone of a polymer by Michael addition polymerization,^[6] which involves the reaction of dithiols with activated dialkenes. The initial polymers we synthesized to demonstrate a proof of concept had poor mechanical properties and did not incorporate a solubility switch.

In a bid to increase the rigidity of the final Michael addition polymer and also to incorporate a solubility switch, dithiol **1** was synthesized according to the procedure outlined in Fig. 3. The alkene was oxidized to the trisulphide with elemental sulfur using a previously described method^[7] The trisulphide was obtained as a mixture of *endo* and *exo* isomers about the carboxy substituent (ratio 1:3) as determined by the presence of two distinct peaks in the gas chromatogram and ¹H NMR spectrum. The isomers were inseparable by column chromatography and the mixture was used for all subsequent reactions. Reduction of the trisulphide was achieved using NaBH₄ in ethanol^[8] to afford dithiol **1** in good yield.

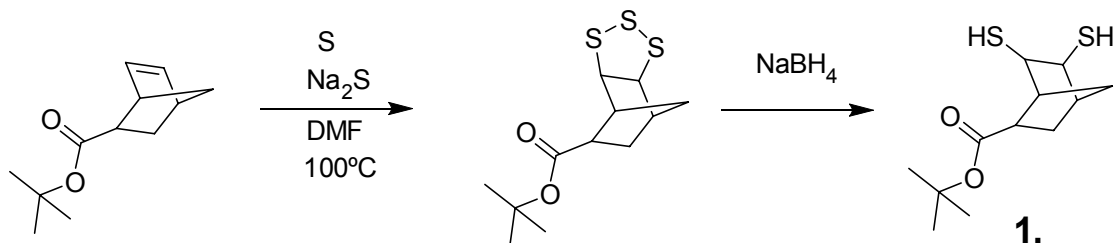


Fig. 3 Synthetic scheme for the synthesis of dithiol **1**.

3.3.3 Synthesis of CP3 via Michael addition

In our proof-of-concept experiments ethylene glycol dimethacrylate (EGDMA) was utilized as a divinyl monomer in the Michael addition polymerization. In this instance we have chosen divinyl sulfone as the second monomer, because it should result in more rigid polymer backbone compared to EGDMA. Reaction of divinyl sulfone with norbornene dithiol monomer **1** at room temperature in the presence of 0.5 equivalents of TEA for 24 hours afforded copolymer CP3 (M_n 17,300; PDI 1.7) as a semi-transparent solid. Since the desired molecular weight was less than 10 k Da modified conditions were employed to reduce the molecular weight closer to this target range. Reaction at room temperature for 4.5 hours gave a lower molecular weight polymer (M_n 3905; M_w 5024; PDI 1.3). This second sample was found by DSC analysis to have a glass transition (T_g) of 140°C. Using ellipsometry the refractive index was found to be 1.8 at 193 nm. The absorbance of this polymer was determined to be 7.2 μm^{-1} . In previous studies we have observed that thioether and sulfone groups do not contribute significantly to polymer absorbance.^[6, 7] Hence, surprisingly high absorbance value was believed to be due to the presence of either low molecular weight impurities or absorbing polymer end groups. This is a matter, which is undergoing further investigation by us.

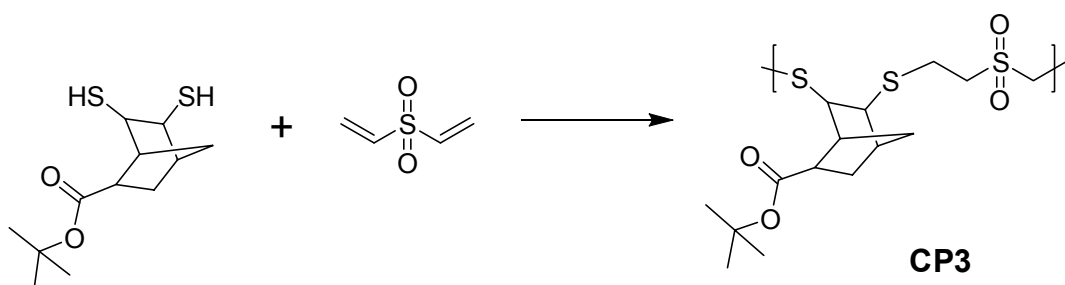


Fig. 4 Synthetic scheme for the Michael addition polymerization of divinyl sulfone and dithiol **1**.

3.4 Imaging of Resist Copolymers

CP1 – CP3 were formulated into resist solutions by dissolving the respective polymer (6 wt%) in PGMEA, along with triphenylsulfonium nonaflate (5 wt % with respect to polymer) and tetrabutyl ammonium hydroxide (0.3 wt% with respect to polymer). The dose to clear curves for CP1 are shown in Fig. 5, for post exposure bake temperatures of 120, 130 and 135°C. Of these temperatures 130 and 135°C were found to clear, although at doses greater than 25 mJ/cm². The slow photo-speed of this system is most likely due to the presence of nitrogen in the monomer structure, which is likely to be acting as a weak base.

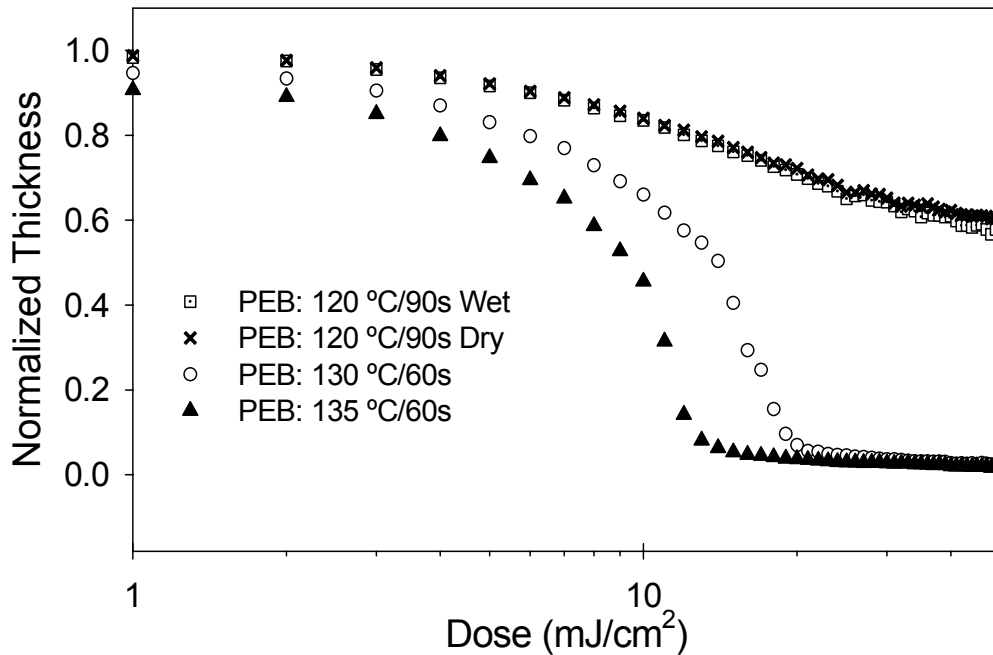


Fig. 5 Dose to clear curves for CP1 for post exposure bake temperatures of 120, 130 and 135°C.

The dose to clear curves for CP2 are shown in Fig. 6 for post exposure bake temperatures of 100, 120 and 130°C, and all PEB temperatures were found to clear, at doses as low as 5.5 mJ/cm². Preliminary dose to clear experiments for CP3 found that an E₀ of 3 mJ/cm² could be obtained. This low E₀ is likely due to high reactivity of the tertiary butyl ester solubility switch compared to the bulky adamantyl leaving group present in CP1 and CP2. Further immersion imaging experiments with CP3 were hampered by interactions between CP3 and standard topcoats.

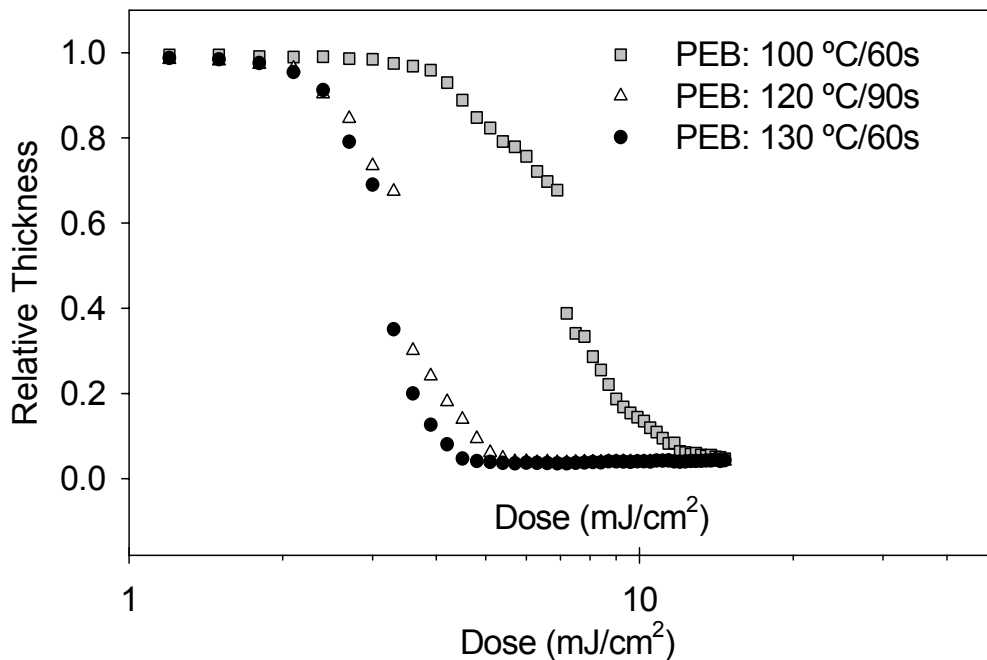


Fig. 6 Dose to clear curves for CP2 for post exposure bake times of 120, 130 and 135°C.

Fig. 7 and Fig. 8 show imaging results for CP2 obtained by water-based 193 nm immersion lithography. Fig. 7 in particular exhibits significant line edge roughness. This is believed to be due to the high molecular weight of the

polymer, *ca.* 68 k Da. Unlike the other monomers utilized in this study, the thiophene based M5 monomer has not acted as a chain transfer agent, which has been our experience for almost all the other sulfur containing monomers that we have studied. We have been able to reduce the molecular weight of CP2 using a thiol based chain transfer agent, which has resulted in molecular weights less than 10k. However, imaging results from these lower molecular weight polymers will be reported at a future date.

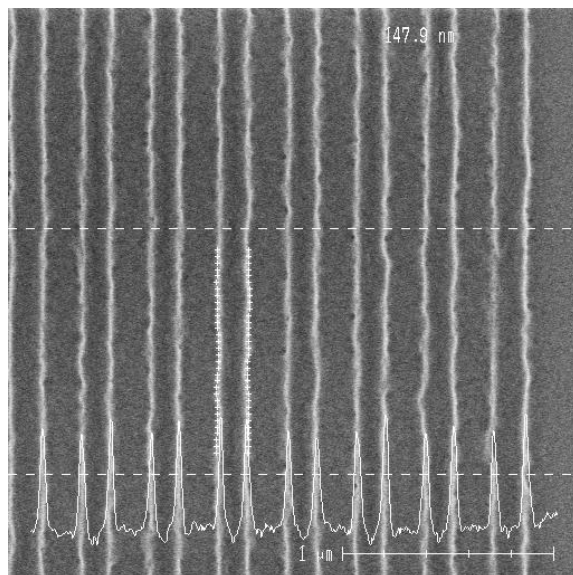


Fig. 7 Imaging results for CP2. Images shows lines patterned at 120 nm pitch.

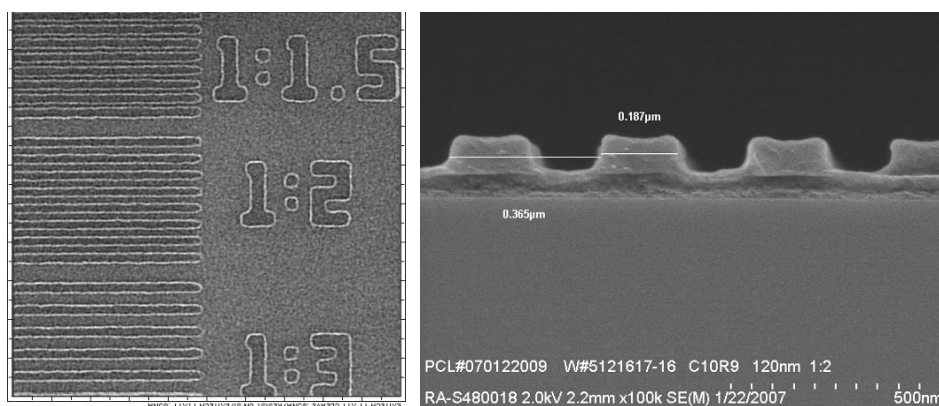


Fig. 8 Imaging results for CP2.

4. CONCLUSIONS

A preliminary QSPR mode has been compiled for predicting the refractive index of small molecules and polymers at 193nm. This model has been used to identify high refractive index targets from databases of commercially available compounds. A series of target monomers were synthesized and their homopolymers prepared by free radical polymerization. The measured RI of these polymers validated the predicted results obtained from the QSPR model. These monomers were also copolymerized with MAdMa to generate polymers with a solubility switch and a high refractive index component. A copolymer with higher sulfur content and a solubility switch was also prepared by Michael addition polymerization. Dose-to-clear experiments demonstrated that a number of these copolymers cleared, although some of the nitrogen containing compounds exhibited slow photo-speed or did not clear at all. Images from water-based 193nm immersion lithography of a high refractive index test resist were successfully obtained.

5. ACKNOWLEDGMENTS

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