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Synthesis of High Refractive Index Sulfur Containing Polymers for 193nm Immersion Lithography; A Progress Report

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ABSTRACT

To be able to extend the 193 nm immersion lithography technology platform, the development of high refractive index immersion fluids and resists is required. This paper reports our investigations into generating high refractive index polymers for use in photoresist formulations for 193 nm immersion lithograph. In this study a series of model compounds have been screened for refractive index and transparency at 589 nm and 193 nm. For the compounds studied this series of experiments demonstrated that sulfur-containing compounds have a positive effect on the refractive index of a molecule at 589 nm. However, the situation is complicated by the presence of absorption bands for some small molecules in the low waveleingth region. To demonstrate this, we examined the refractive index dispersion of a series of molecules based on ethyl acetate with varying degrees of sulfur substitution. These results indicated that an anomalous increase in refractive index could be expected 20 - 30 nm above the absorption maximum. The implications for design of high refractive index resists for 193 nm immersion lithography are discussed.

Keywords: Immersion lithography, resist polymers, high RI, RI dispersion, sulfur, QSPR

1. INTRODUCTION

Immersion photolithography at 193 nm has been confirmed to a viable technology for integrated circuit manufacture at the 65 nm and 45 nm nodes. Advances in immersion fluid and resist design could extend 193 nm immersion lithography to the 32 nm node or below. 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,[1-3] with the aim of increasing the numerical aperture of a system, in turn leading to reduced the possible feature sizes. Furthermore, it is anticipated that the development of second[4] and third generation fluids over the next several years will enable the 32 nm node. An additional advantage of an increased RI of the fluid is the gain of an increase in the depth of focus of the process.

Likewise significant improvements to immersion lithography are expected when the RI of the resist is increased beyond the current average value of 1.65. Specifically, it has been shown that an increase in the RI of the polymeric resist will result in an increase in the depth of focus and hence exposure latitude.[5] We have recently reported on the design and synthesis of novel polymers with increased RI for use in future immersion resist formulations.[6] Significant gains in RI for the next generation of resists are reported here. An example of a high refractive index polymer we have synthesized previously has give in **Error! Reference source not found.**. An essential part of the discovery process is the use of a quantitative structure-property relations (QSPR)[7,8] model developed by us to predict the refractive index of small molecules and polymers.[9] In this model a set of nine descriptors were determined to describe the RI of a large dataset of

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molecules at 589 nm. The high correlation between the predicted and experimental RI at 589 nm using this model is depicted in Figure 1. Those candidate molecules with high refractive index at this wavelength are, in the absence of intense absorption bands, expected to also have high values of RI at 193 nm. Candidate molecules are thus screened using this model and those with high values of RI at 193 nm considered for placing in the synthetic program.

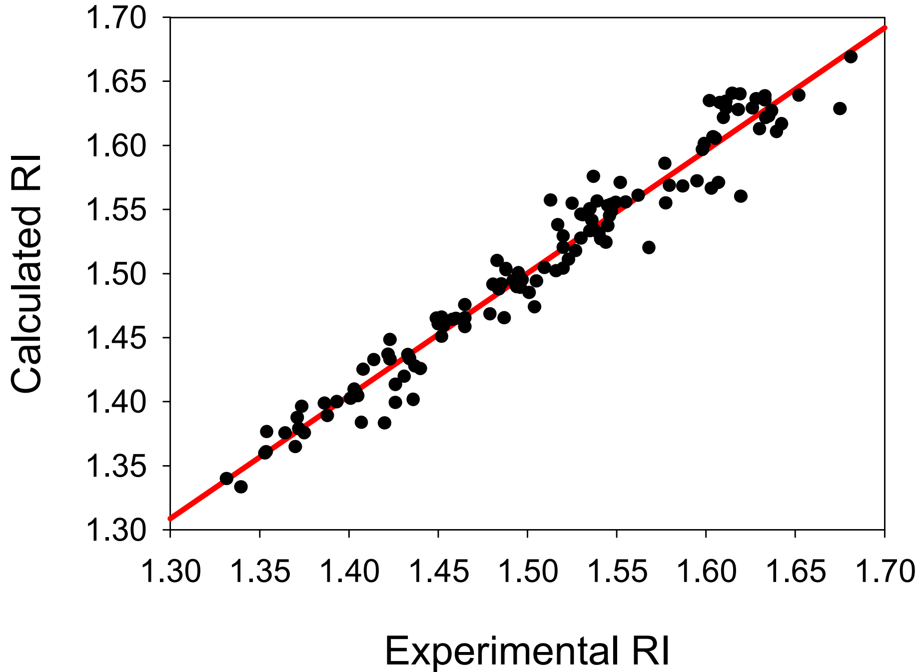

Figure 1. Comparison of values of refractive index (RI) at 589 nm determined experimentally with those calculated using the best nine-parameter QSPR model.[9]

An alternative approach to obtaining increases in RI at low wavelengths is to exploit the anomalous dispersion of the refractive index close to an intense absorption line. The refractive index and absorbance are generally related by the Kramers-Kronig relation, and hence at wavelengths immediately above the absorbance maximum anomalously-high values of the refractive index are observed. The possibility of exploiting this phenomenon in the design of high-RI resist polymers is explored in this paper.

2. METHODOLOGY

2.1 Materials

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

2.2 Monomer Synthesis

Synthesis of S-(tert-butoxycarbonyl)methyl O-ethyl carbonodithioate ***(1)****:* tert-butyl 2-chloroacetate (27 mmol) was dissolved in dichloromethane (25 mL), potassium O-ethyl carbonodithioate (25 mmol) was dissolved in distilled water (25 mL). The organic and aqueous phases were combined to give a two-phase system. The aqueous phase was yellow and the organic phase colourless. Aliquat 336 (0.2 g), a phase transfer catalyst, was added to the system. The system was allowed to react overnight at 25 °C with magnetic stirring. After reaction the aqueous phase was colorless and the organic

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phase was yellow. The organic layer was separated, concentrated and diluted with diethyl ether. The organic phase was extracted with distilled water (x 3). The organic extract was then concentrated, purified by passing it through a basic alumina column, 50:50 hexane : ethyl acetate. A yellow oil **(1)** was isolated (95%).

*Synthesis of tert-butyl 2-mercaptoacetate **(2)**:* **(1)** (19 mmol) and 1-aminopropan-2-ol (21 mmol) were dissolved in dichloromethane (20 mL). The reaction was purged with nitrogen. The reaction was kept at room temperature and stirred for 3 hours. Following the reaction the mixture was concentrated and diluted with diethyl ether. This organic fraction was washed with 0.1 M HCl (x 3) and finally with distilled water (x 3). The organic fraction was concentrated, purified by column chromatography and by vacuum distillation. **(2)** was isolated as a pungent colorless oil (71%).

*Synthesis of (tert-butoxycarbonyl)methyl thiomethacrylate **(3)**:* **(2)** (12.5 mmol) and triethylamine (12.5 mmol) were dissolved in dry dichloromethane (10 mL). Under an atmosphere of nitrogen and at a temperature of approximately 0 °C, methacryloyl chloride (12.5 mmol) was added dropwise over 10 minutes with stirring. Following addition the reaction was allowed to warm to 25 °C, and the reaction was allowed to continue for 3 hours. The precipitated TEA salt was separated by filtration and the filtrate was concentrated and diluted with diethyl ether. The mixture was then washed with 0.1 M HCl (x 3), 0.5 M sodium bicarbonate and finally with distilled water (x 3). The organic layer was concentrated and the product was purified by vacuum distillation. The colorless oil **(3)** was isolated (55%). NMR

*Synthesis of tert-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate **(4)**:* Freshly cracked cyclopentadiene was added dropwise to a stirred mixture of tert-butyl acrylate abd saturated brine solution. Following addition of cyclopentadiene the reaction was allowed to react for 16 hrs at 25 °C. Reaction mixture was extracted with diethyl ether (x 3). The combined organic fractions were concentrated and purified by column chromatography, 95:5 hexane : ethyl acetate. A colourless oil **(4)** was isolated (94%).

*Synthesis of tert-butyl 5-(2-hydroxyethylthio)bicyclo[2.2.1]heptane-2-carboxylate **(5)**:* mercaptoethanol (17.4 mmol) was added dropwise to **(4)** (16.5 mmol) over 30 min at a temperature of 0 °C. The reaction mixture was washed with 0.5 M sodium bicarbonate (x 3) and distilled water (x 3). The product was purified by column chromatography (Al2O3) (50:50 hexane : ethyl acetate). A colourless oil was obtained (96%)

*Synthesis of tert-butyl 5-((2-(methacryloyloxy)ethyl)sulfanyl)bicyclo[2.2.1]heptane-2-carboxylate**(6)**:* Methacryloyl chloride was added dropwise to a solution of **(5)** and triethylamine in dichlomethane, under a nitrogen atmosphere at 0 °C. The reaction workup was as for **(3)** except that the monomer was not purified by vacuum distillation. A colourless oil was obtained (86%).

2.3 Polymer Synthesis

Both monomers were polymerized separately via conventional radical polymerization. The initiator was 1% AIBN, and the solvent was tetrahydrofuran at 60°C. After 16 hours the resulting polymers were precipitated in methanol (x 3).

2.4 Analysis

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

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.

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3. RESULTS AND DISCUSSION

3.1 Modelling of RI Dispersion

Previously we have described methods based on QSPR to predict the refractive index of monomers and polymers *at 589 nm*.[9] The best QPSR model determined from a database of over 120 compounds was able to accurately predict the refractive index of an external set of molecules that had not been used to develop the model. However, for the QSPR model to be useful in predicting the RI of small molecules and polymers at 193 nm, we require accurate methods for predicting the RI dispersion across a large range of wavelengths. Our approach has been to use the Lorentz-Lorenz equation to calculate the refractive index dispersion (see equation 1).

$$\frac{n^2-1}{n^2+2}V = \frac{4}{3}\pi N\alpha \qquad (1)$$

In this equation $\boldsymbol{n}$ is the refractive index, $\boldsymbol{V}$ is the molar volume, $\boldsymbol{N}$ is Avogadro's number, and α is the polarizability. The molar volume and polarizability have been calculated using the Gaussian software package.

Examples of comparisons of the calculated RI dispersion with the experimental data are shown in Figure 2 and 3. The calculations shown as full circles in Figure 2 are in excellent agreement the experimental data. Hence, for these compounds the QSPR in combination with modelling of the RI dispersion can be used to predict the refractive index at 193 nm. However, the calculated data shown in Figure 3 is not in good agreement with the experimental results; the reason for this is that the RI dispersion for these molecules deviates from a typical Cauchy relation in the UV region. This atypical dispersion is due to the compounds absorbing in this wavelength region. Hence, at this stage it is not possible for us to predict the refractive index of compounds that exhibit absorption bands at 193 nm using the QSPR/ RI dispersion modelling approach. To overcome this deficiency we have adopted several approaches; we are seeking to calculate the location of absorption bands around 180-200 nm. In addition a QSPR model derived from values of refractive index measured at 193 nm is in the process of being developed.

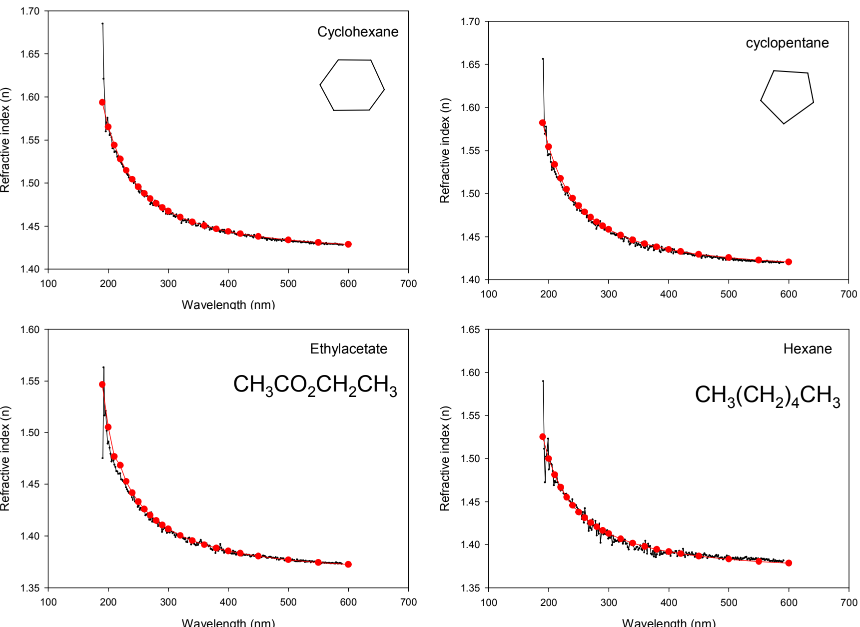

Figure 2. Comparison of calculated and experimental RIs for compounds exhibiting no absorbance.

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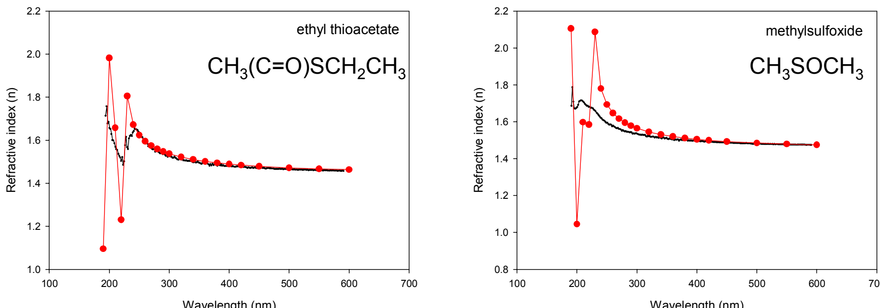

Figure 3. Comparison of calculated and experimental RIs for compounds exhibiting absorbance bands.

3.2 RI and Absorbance Measurements of Model Compounds in the UV region

Table 1 shows a selection of structures, with RI values at 193 nm and 589 nm, and an indication of the absorbance at 193 nm. For the data at 589 nm the results reflect the findings from the QSPR model generated for predicting RI of organic compounds at 589 nm, i.e. that sulfur-containing compounds have a high refractive index and that polarizable groups such as aromatic groups also increase the RI at 589 nm. However, if we compare the RI of the compounds at 589 nm and 193 nm, we can see that a high refractive index at 589 nm does not necessarily precict to a high refractive index at 193 nm. For example, the compounds that exhibit high absorbance at low wavelengths, such as the aromatic-containing compounds and ethyl dithioacetate do not have a high RI at 193 nm. A number of trends can be observed in the data at 193 nm. The RI of the linear alkane hexane is 1.47 at 193 nm. We can see from table 1 that compared to their linear analogues, cyclic compounds tend to have a higher refractive index by approximately 0.1 units. For example, the RI of cyclohexane is 0.12 higher than hexane, and butyrolactone has a RI 0.11 units higher than ethyl acetate. Thioether compounds also lead to higher refractive indices compared to the alkane analogues. For example, bis(methylthio)methane, a compound with two thioether functional groups, has an RI of 1.9 compared to hexane which has an RI of 1.47. 1,4-oxathiane which has one ether and one thioether group has a RI of 1.79 compared to cyclohexane which has a RI of 1.59. Another important point to make is that the aromatic compounds in this study exhibited large absorption bands at 193 nm and are consequently unsuitable to be included as components in photoresists. To summarize, some of the important findings from this set of model compounds are:

- linear alkanes have a base RI of 1.47
- cyclic compounds have values of RI approximately 0.1 higher than the linear analogues
- thioethers result in significant increases in RI compared to non-sulfur containing analogues
- aromatics groups lead to high absorbance at 193 nm

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Table 1. RI data at 193 and 589 nm for a series of model compounds considered in this study.

Compound	193 RI	589 RI	k	Compound	193 RI	589 RI	k
	1.4725	1.38	very low		1.9	1.5265	low
	1.5951	1.4284	very low		1.7879	1.5004	low
	1.5695	1.4124	very low		1.7291	1.5083	low
	1.6252	1.4334	very low		1.725	1.5818	high
	1.5166	1.373	very low		1.745	1.5575	high
	1.7136	1.4584	low		1.5252	1.3985	very low
	1.5825	1.5599	high		1.4249	1.3456	very low

The effect of substitution of sulfur in the series ester/thioester/dithioester is more complicated. Figure 4 shows the RI and absorbance data for a series of ethyl acetate derivatives that contain different amounts of sulfur. Ethyl acetate shows only a small increase in absorbance with decreasing wavelength. Ethyl acetate also exhibits a typical RI dispersion, which can be accurately fitted to the Lorentz-Lorenz equation. In comparison, ethyl thioacetate has an absorption band at approximately 230 nm, and at 193 nm appears to be on the edge of a adsorption band situated at a lower wavelengths. When the refractive index disperse is compared to the absorbance there appears to be an anomalous increase in the RI resulting from only a slight increase in the absorbance. Finally, ethyl dithioacetate has strong absorption bands at 310 and 210 nm. At 193 nm the ethyl dithioacetate has a relatively low refractive index due to the proximity of the absorption band maximum.

The anomalous dispersion of the ethyl thioacetate indicated that high RI could be achieved without compromising transparency, and hence we have decided to synthesize a range of thioester-containing monomers and polymers.

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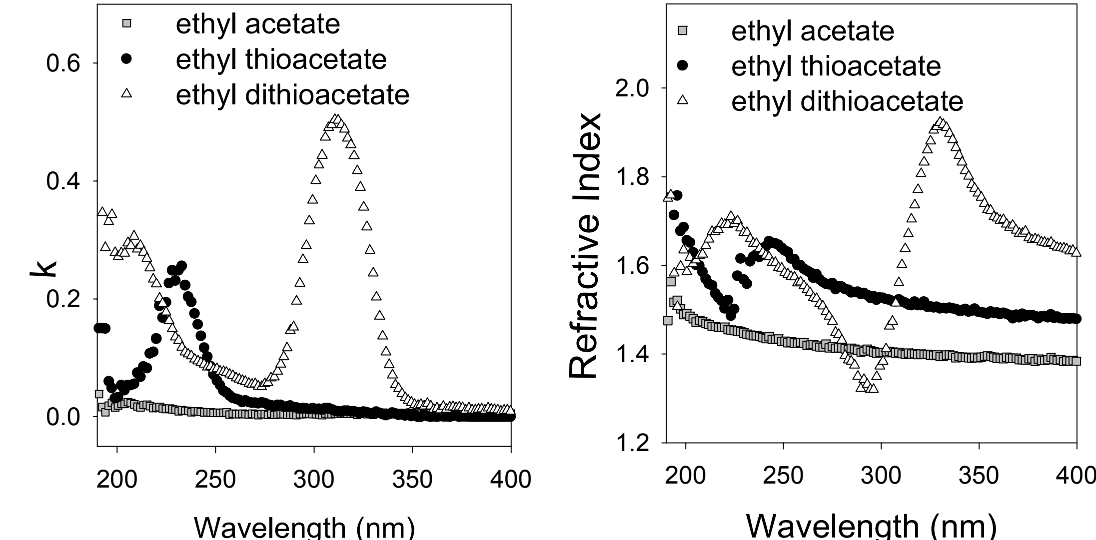

Figure 4. Absorbance (k) and refractive index (n) versus wavelength for a series of molecules containing varying amounts of sulfur.

3.3 Monomer and Polymer Synthesis

The scheme for the synthesis of the thiomethacrylate monomer **(3)** is depicted in Figure 5. The synthesis involved reaction of tert-butyl chloroacetate to form **(1)**. Molecule 1 was reacted with 1-aminopropan-2-ol to generate the thiol **(2)**. Thiol **(2)** was then reacted with methacryloyl chloride in the presence of triethylamine to generate the thiomethacryalte **(3)**. To obtain a polymer **(7)** thiomethacrylate **(3)** was polymerized by free radical polymerization using AIBN as an initiator and the structure of the polymer is depicted in Figure 7.

Cl O O K+ S S− O S 1 O O S S NH2 OH OH H N O S + HS O O 2 Cl O TEA O S O O 3

Figure 5. Synthetic scheme for synthesis of monomer 3.

The scheme for the synthesis of monomer **(6)** is depicted in Figure 7. Freshly cracked cyclopentadiene underwent a Diels Alder reaction with tert-butyl acrylate to form **(4)**, a norbornene derivative. Molecule **(4)** underwent a Michael-addition reaction with mercaptoethanol to generate a thioether-containing molecule **(5)** and this was converted to a methacrylate **(6)** by reaction with methacryloyl chloride in the presence of TEA. Monomer **(6)** was polymerized to give **(8)** by conventional free radical polymerization using AIBN as an intiator. The structure of the polymer is depicted in Figure 7.

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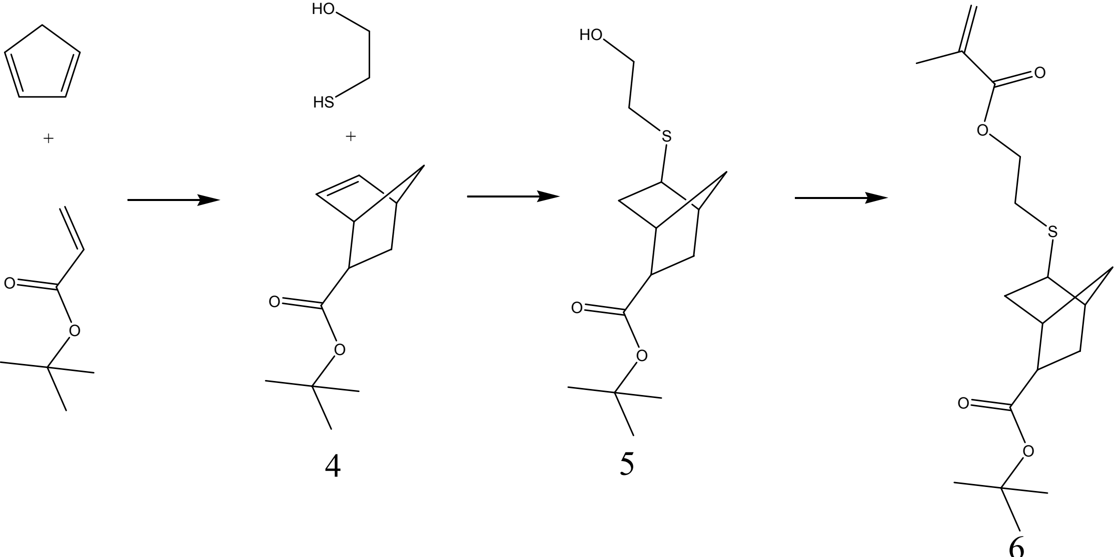

Figure 6. Synthetic scheme for synthesis of monomer 6.

Figure 7. Structures of polymers 7 and 8 prepared in this study.

3.4 RI Measurements of the Polymers

Figure 8 shows the refractive and absorbance dispersion for the polythiomethacrylate **(7)** and for ethyl thioacetate. The absorbance dispersion of polymer **(7)** is similar to the model compound ethyl acetate, with the absorbance band at approximately 230 nm being slightly red shifted. The RI data for polymer **(7)** also exhibits a similar profile to the model compound. In particular the anomalous increase in the RI between 220 and 190 nm is replicated in the polymer. The refractive index of polymer **(7)** was measured to be 1.81 units, which is 0.1 units higher than the model compound. This increase is due primarily to the increase in density that occurs during polymerization. The sulfur content of this polymer is 15%.

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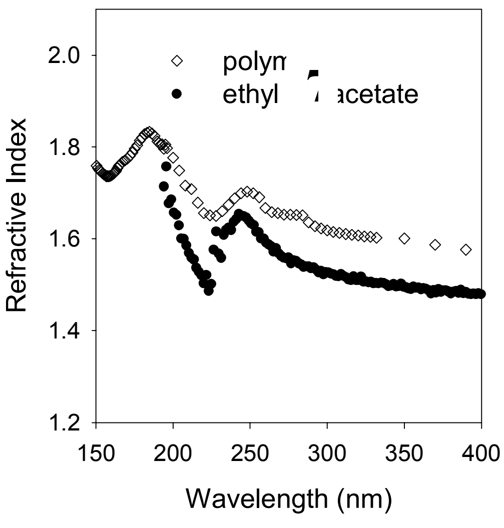

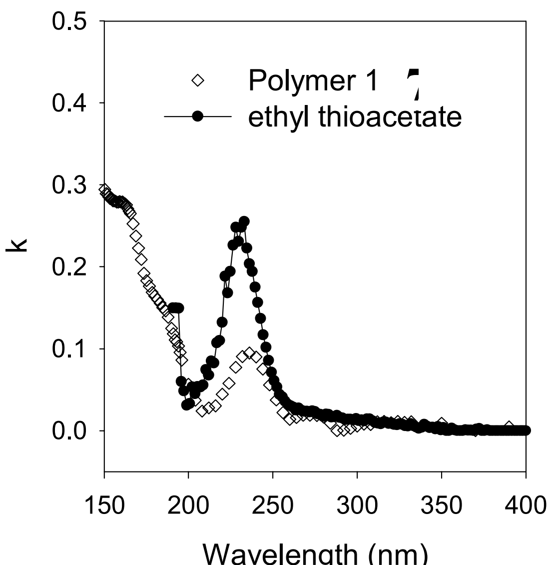

Figure 8. Absorbance (k) and refractive index (n) versus wavelength for polymer 7 and ethyl thioacetate.

Table 2 lists the refractive indices for a series of polymers that have synthesized in our laboratories. Polymer A is a polymer that we have previously reported.[9] Polymer (**7**) is the polythiomethacrylate described above. Polymer (8) is the thioether compound shown in Figure . Polymer (**8**) has a refractive index of 1.74 and an absorbance (k) value of 0.04; the sulfur content of this polymer is 9.8%.

Table 2. Values of RI for synthesized polymers.

Polymer	**RI at 193 nm**
1 (Std ArF resist Polymer)	1.7
Polymer A	1.88
Polymer (7)	1.81
Polymer (8)	1.74

4. CONCLUSIONS

We have demonstrated that it is possible to model the refractive index dispersion of non-absorbing compounds using the Lorentz-Lorenz equation and values of polarizability and molar volume calculated using the Gaussian software package. Hence, using a QSPR model to predict refractive index at 589 nm it is possibly to accurately predict the RI at 193 nm. However, this is not possible for molecules that have absorbance bands in the area of interest. We are currently in the process of developing methods to accurately predict the absorbance of molecules and also of developing a QSPR model using data collected at 193nm; this data is currently being collected. Some of the initial results from this data set have been presented and the general trends indicate that thioether, thioester and cyclic compounds increase the RI at 193 nm and that aromatics and dithioesters have significant absorption bands in this region making them unsuitable for lithographic applications. Thioether and thioester monomers were synthesized and polymerized to demonstrate that their synthesis was possible. The refractive indices of these polymers was found to be greater than that of a standard ArF resist.

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