Polymer Matrix Effects on the Photochromic Interconversion of Perfluorodiarylethenes

Richard P. Kingsborough,* Theodore H. Fedynyshyn, Vladimir Liberman, and Alberto Cabral
MIT Lincoln Laboratory, 244 Wood St. Lexington, MA 02420

Abstract. Absorption modulation optical lithography (AMOL) is a potentially lower cost photolithographic technique that relies on the modulation between two absorbance states of a photochromic compound embedded within a polymer matrix. Current processing requires the use of a barrier layer to prevent intermixing of the AMOL layer with the photoresist. We have investigated the use of other polymer matrices in order to provide flexibility when choosing the AMOL layer to remove the need for the barrier layer, reducing processing steps. We have characterized two photochromic compounds in polymers of three different polarities and solvent requirements. We have found that the quantum yield of photoconversion is highly dependent on the dipole moment of the polymer matrix.

Introduction

Photochromic compounds embedded within a polymer matrix have been investigated as materials for absorbance modulation optical lithography (AMOL). In this technique, a thin film of photochromic material is deposited over a photoresist layer. These photochromic compounds can undergo a light-induced reversible molecular transition between two different isomers (Fig. 1). By using interference lithography with two wavelengths that cause the photoconversion with a pattern that overlaps the peaks at $\lambda_1$ with the nodes at $\lambda_2$, an image can be transferred to an underlying photoresist. The absorption at $\lambda_1$ results in the photoisomer that is transparent at $\lambda_1$, but the regions exposed to $\lambda_2$ revert to the original photoisomer and continue to absorb at $\lambda_1$, effectively acting as a photomask. Only at the $\lambda_2$ nodes does a transparent aperture form.

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One of the classes of compounds that exhibit this behavior are the diarylethenes, specifically perfluorodithienoethenes (Fig. 2). The dithienoethene 2 in Fig, where Ar = 5-methyl-2-thienyl, was previously investigated as an AMOL layer when cast in a PMMA film doped with the photochromatic compound on top of a photoresist layer.² The absorption spectra of this compound allowed for the use of a He-Cd laser (325 nm) and a He-Ne laser (633 nm) for the \( \lambda_1 \) and \( \lambda_2 \) wavelengths, respectively. One drawback to this approach, however, as that the solvent used for the AMOL layer deposition affected the development rate of the underlying photoresist. In this case, a thin polyvinyl alcohol (PVA) layer was deposited between the photoresist and the AMOL layers to prevent the intermixing. This added an additional processing step and the PVA layer needed to be sufficiently thin to prevent line blurring.

One solution to the intermixing problem is to incorporate the photochromic compounds in other polymeric matrices in which the casting solvent does not allow for intermixing between the AMOL and photoresist layers. In this paper, we have incorporated two different photochromic compounds 1 and 2 in three different polymer matrices with varying polarities to determine the effects of the local chemical environment on the quantum yield of the photoconversion processes. We find that there is a strong correlation between the dipole moment of the polymer matrix and the quantum yields of the two processes.
**Experimental**

All chemicals and polymers were obtained from Aldrich unless noted and were used as received. Bleaching and coloration kinetic experiments were performed on ~200 nm thick polymer films containing 25 wt% of compounds 1 and 2 in the chosen polymer matrix. The films were spin coated onto 1” quartz discs and were baked at 120 °C for 60 sec to remove residual solvent. The coloration reactions were carried out using a He-Cd laser (325 nm, 8 mW) and the bleaching reactions were carried out with a He-Ne laser (633 nm, 25 mW). Reaction kinetics were monitored using an Ocean Optics UV-vis spectrometer with a 550 nm band pass filter and monitoring the absorbance change at 580 nm or 611 nm ($\lambda_{\text{max}}$ for 1o and 2o, respectively). A schematic of the measurement setup is shown in Fig. 3. Exposure doses were measured by a Coherent high sensitivity thermopile sensor power meter. The Dill C parameter$^5$ was extracted from a plot of transmission vs. exposure dose using a ProABC software package.$^6$

![Fig. 3 Schematic of experimental setup for measuring photokinetics.](image)

**Results and Discussion**
Photochromic phenyl-substituted compound 1o was synthesized according to Scheme 1 in which 2-chloro-5-methylthiophene was first brominated in acetic acid to afford 2-chloro-4-bromo-5-methylthiophene. Lithiation of the bromothiophene and quenching with perfluorocyclopentene afforded the chloro-terminated perfluorodithienylethene, which was subsequently converted to the phenyl-substituted 1o via a Suzuki coupling with phenylboronic acid. Compound 2o was synthesized via literature methods according to Scheme 2. Dibromination of 2-methylthiophene in dioxane, followed by a Kumada cross coupling of 5-methylthiophen-2-yl magnesium bromide, generated in situ from 2-bromo-5-methylthiophene in diethyl ether, afforded 4-bromo-5,5-dimethyl-2,2′-bithiophene. Lithiation and quenching with perfluorocyclopentene afforded 2o. NMR and UV-vis spectra were consistent with the formation of both 1o and 2o.

In order to be useful absorbance modulating layers for lithographic applications, the photochromic compound was embedded in a variety of different polymer films that could be deposited from solvents which would not intermix with an existing photoresist layer. Fig. 4 shows the polymer matrices used in this study. The polymers varied in polarity from polystyrene (PS) to poly(methyl methacrylate) (PMMA) to poly(2-hydroxyethyl methacrylate) (PHEMA). Compounds 1o and 2o were combined with a given polymer in an appropriate solvent and at a solids content such that, when spin coated as a thin film (ca. 200 nm), the resulting films had a roughly 90% transmission on a quartz substrate at $\lambda_{\text{max}}$. 
The resulting polymer-composite films were fully converted to the closed state from the initial as-spin coated state by exposure to a 325 nm laser in a custom exposure setup. Spectra of I and 2 in a PMMA matrix are shown in Fig. 5a. The UV-vis spectra of I and 2 in the other matrices are remarkably similar (Table 1). The kinetics of the closed to open conversion were monitored using an Ocean Optics spectrometer positioned in line with the exposure laser (Fig. 3) by monitoring the absorbance of the $\lambda_{\text{max}}$ of Ic and 2c (580 nm and 611 nm, respectively, Fig. 5a). A UV-vis spectrum of the fully closed film was then recorded. The fully closed Ic and 2c films were then exposed to 633 nm irradiation and the kinetics were again monitored as a function of exposure dose, Error! Reference source not found.b. This process required a much higher exposure dose due to the lower quantum yield of this process, which has been observed in similar photochromic systems by others.11 Once fully opened, a second UV-vis spectrum was recorded (Fig. 5a). The full kinetics of the 2o to 2c process were then monitored by reexposing the 1o and 2o composite films at 325 nm in order to accurately measure the kinetics from a fully open form of the photochromic 2, Error! Reference source not found.c.
Fig. 5  (a) UV-vis spectra of perfluorodiarylethenes 1 and 2 at 25 wt % loading in PMMA on quartz substrates. (b) Ring opening (b) and closing (c) kinetics of 1o and 2o in PMMA matrices at 25 wt % loading after exposure to 633 nm (b) or 325 nm (c) light. The absorbance of 1o and 2o at 580 nm and 611 nm, respectively, was used to monitor the photochemical kinetics.
Once the data was collected, the Dill C parameter\(^5\) was extracted from a plot of transmission vs. exposure dose using a ProABC software package.\(^6\) In this instance, the Dill C parameter is the kinetic rate constant for the conversion of the photochromic material between its open and closed forms. The quantum efficiency of the photointerconversion is a ratio between the number of molecules converted between the open and closed forms and the number of photons absorbed. By using the experimentally determined Dill C value, we can calculate the quantum yield of both photointerconversions through the use of Equation (1), where \(\Phi\) is the quantum yield, \(N_A\) is Avogadro’s number, \(MW\) is the molecular weight of the perfluorodiarylethene, \(h\) is Planck’s constant, \(c\) is the speed of light, \(C\) is the exposure rate constant (Dill’s C), \(a\) is the absorption coefficient (\(\mu m^{-1}\)), and \(\lambda\) is the exposure wavelength.\(^\text{12,13}\)

\[
\Phi = \frac{C N_A h c}{a \lambda (MW)}
\]  

(1)

The ring-closing process for \(1o\) had lower quantum yields than for the corresponding compound in hexane\(^\text{11}\) or acetonitrile\(^\text{14}\) solutions (Table 1). This may be due to the constraints placed on the molecule in the solid state versus the free rotation found in solution. The corresponding solution quantum yield data for compound 2 have not been measured. The quantum yields of the opening and closing processes were dependent on the polarity (dipole moment) of the polymer matrix in a similar fashion to solution behavior of similar photochromic complexes.\(^\text{15}\) Irie and co-workers\(^\text{15}\) discuss how the polarity of the various solvents affects the transition state during the cyclization process. Although we have not found another report of photochromism being investigated in multiple polymer matrices, we believe that the same effect of polarity on the transition states is also present in polymer materials.

The quantum yields for the ring closing process were determined to be inversely related to increasing dipole moment of the polystyrene\(^\text{16}\), PMMA\(^\text{17}\), and PHEMA\(^\text{18}\) polymer matrices (Fig. 6). The opposite trend is observed for the opening process. It seems that the ring closing process in both 1 and 2 is suppressed as the polarity of the polymer matrix increases, while a polar environment is favorable for the ring opening process.

Table 1 Polymer matrix effects.

<table>
<thead>
<tr>
<th>Polymer Matrix</th>
<th>Dipole Moment</th>
<th>(\lambda_{\text{max, o}}) (nm)</th>
<th>(\lambda_{\text{max, c}}) (nm)</th>
<th>(\phi_{1o \rightarrow 1c})</th>
<th>(\phi_{1c \rightarrow 1o})</th>
<th>(\lambda_{\text{max, o}}) (nm)</th>
<th>(\lambda_{\text{max, c}}) (nm)</th>
<th>(\phi_{2o \rightarrow 2c})</th>
<th>(\phi_{2c \rightarrow 2o})</th>
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</thead>
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<tr>
<td>pHEMA</td>
<td>3.2</td>
<td>288</td>
<td>591</td>
<td>0.289</td>
<td>6.26 \times 10^{-3}</td>
<td>322</td>
<td>611</td>
<td>0.181</td>
<td>4.6 \times 10^{-4}</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.457</td>
<td>281</td>
<td>589</td>
<td>0.343</td>
<td>4.21 \times 10^{-3}</td>
<td>319</td>
<td>611</td>
<td>0.199</td>
<td>3.7 \times 10^{-4}</td>
</tr>
<tr>
<td>PS</td>
<td>0.36</td>
<td>286</td>
<td>590</td>
<td>0.419</td>
<td>3.86 \times 10^{-3}</td>
<td>322</td>
<td>611</td>
<td>0.296</td>
<td>3.0 \times 10^{-4}</td>
</tr>
</tbody>
</table>
Conclusions

We have incorporated photochromic compounds into polymer matrices and investigated their photochromic behavior as thin films spun cast onto quartz substrates. The differing polarities of the polymer matrices do not appear to shift the chromophore of the open or closed forms of the photochromic compounds, indicative of less of an immediate interaction with their chemical environment. There is, however, a striking dependence on the speed and quantum yield of the ring-closing process on the polarity (dipole moment) of the polymer matrix. This greatly influences the exposure dose required to affect a complete conversion to the closed form and informs the throughput of any potential photolithographic application of an AMOL layer for low cost photoresist patterning.

References


**Fig. 1** Quantum yield vs. polymer matrix dipole moment for dithienylethenes 1 (●) and 2 (▲) after exposure to 325 nm (●, ○) and 633 nm (▲, △) light.


