Light-Induced Reversible Volume Changes in Thin Films of Azo Polymers: The Photomechanical Effect

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ABSTRACT: A light-induced expansion of thin films of polymers containing azobenzene chromophores was characterized in real time by single wavelength ellipsometry. An initial expansion of the azo polymer films was found to be irreversible with an extent of relative expansion observed of 1.5−4% in films of thickness ranging from 250 to 1400 Å. A subsequent and reversible expansion was observed with repeated irradiation cycles, achieving a relative extent of expansion of 0.6−1.6%. Control over the extent of this reversible expansion was achieved by varying the pump beam power or irradiation duration, allowing these polymers to function as reversible photomechanical materials.

Introduction

Thin films of azobenzene (azo)-containing polymers have many potential applications as photoactive materials for micropatterning,[1] for reversible optical storage,[2,3] and as sensors,[4−7] based on the light-activated interconversion between the two geometrical isomers. The photochemical *trans*-to-*cis* isomerization and the thermal or photochemical back-conversion to the energetically favored *trans* isomer are well-studied phenomena.[8,9] The photoinduced *trans−cis* isomerization generally takes picoseconds to milliseconds to complete in solution,[10,11] while the thermal relaxation from *cis* to *trans* is a slower process that requires tens of seconds to many hours depending on the chromophore[12] and the nature of the polymer backbone.[13,14] Although the photochemical *trans*-to-*cis* isomerization of azobenzene has been well studied for nearly 50 years,[15] many interesting questions concerning the behavior of polymeric azo systems remain unanswered. For example, spin-cast films of azo polymers have been found to produce surface relief gratings (SRGs) when exposed to interfering laser irradiation,[16−18] whereby the polymer moves across a surface in response to light of certain polarizations. The mechanism of the mass transport well below T_g is still unresolved, but it has been suggested that the formation of SRGs is possibly due to a photoexpansion effect.[19,20] Recently, similar interest has been given to the photodeformation properties of other azo thin films, such as studies with free films of azo-polyester which have shown macroscopic deformation upon irradiation with low power circularly polarized light for both amorphous or liquid crystalline polymers.[21] Last, Ikeda and co-workers have also demonstrated a light-induced bending of free-standing liquid-crystal network azo films, whereby light impinging on the surface causes the material to bend and curl along the polarization director, relaxing back to flat when the *cis*-to-*trans* back-isomerization is activated at a different wavelength.[22,23] Despite some similarities to previous observations of photochemically induced free volume changes in azo films measured by ellipsometry[24] or by total attenuated reflection,[25,26] no current explanation for a mechanical force at the molecular level exists for the phenomena of both SRG photoinscription and LC film curling. In addition to any fundamental insight to be gained from a detailed study of this effect, an understanding of the photoexpansion behavior of these azo polymer systems might provide development of some interesting applications based on this piezoelectric-like response, such as photoactuation or artificial muscles. In this paper, we use null ellipsometry to confirm a photomechanical response in azo polymers directly for the first time and then characterize this photomechanical effect for thin films poly-Disperse Red 1 acrylate (PDR1A) and copolymers of acrylic acid (AA) with varying dye content, under various irradiation conditions and film thicknesses. In addition to providing a thorough characterization of the photomechanical effect for development of future photomechanical materials, this work also allows insight into the previously unresolved mechanisms of light-activated material response, such as LC film bending and the mass transport effect of SRG formation.

Experimental Section

Materials. A copolymer series of poly-Disperse Red 1 acrylate (PDR1A) and acrylic acid (AA) as shown in Figure 1 was synthesized by free radical polymerization.[27] Thin films of PDR1A and copolymers were prepared by spin-coating (1300 rpm) from solutions made from distilled tetrahydrofuran onto polished ⟨100⟩ silicon wafers. The films were annealed under vacuum for 8 h at 110 °C.

Photoexpansion. The thickness and refractive index changes of the azo films were measured using a Multiskop single wavelength (633 nm) null ellipsometer (Optrel, Germany) at a fixed angle of incidence (70°). Although the He−Ne laser of the measuring beam is far from the absorption maximum of PDR1A, the power was attenuated by a 2.0 O.D. filter to further minimize any induced photoorientation during the measurements. The irradiation (pump) beam at $\lambda = 514$ nm was obtained from an Ar+ ion laser. The beam was expanded to a diameter of 5.0 mm with a series of lenses in order to ensure that the probe beam cross section (2.3 mm) was completely irradiated. The pump beam was arranged to be incident normal to the plane of the film and so that the pump beam coincides with the rotational axis of the goniometer. The pump beam was circularized with a quarter-wave plate to ensure that no in-plane photoalignment of the azo chromophore occurred. The power of the pump beam (0.7−215 mW/cm²) was varied by attenuation with neutral density absorbance filters.

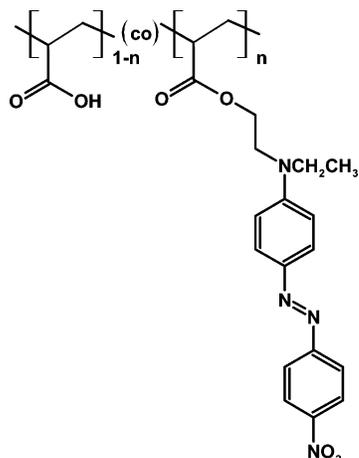* To whom correspondence should be addressed. E-mail: christopher.barrett@mcgill.ca.

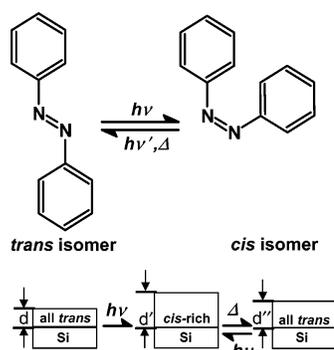**Figure 1.** Chemical structure of poly(DR1A-*co*-AA) where n = 1, 0.35, and 0.05.

Figure 2. An illustration of photochemical induced *trans*-to-*cis* isomerization of azobenzene and a schematic representation of the photoexpansion effect in poly(DR1A-*co*-AA) thin films where the thickness $d' > d'' > d$.

Figure 3. Typical initial expansion and relaxation curve for 100 mol % PDR1A with a 30 s pump beam irradiation at 514 nm with a beam intensity of 207 mW/cm^2, showing a saturation of thickness increase in the first pump cycle and a relaxation in the dark.

Figure 4. Typical reversible expansion and relaxation curve for 100 mol % PDR1A, with three 30 s pump cycles irradiated at 514 nm with a beam intensity of 207 mW/cm^2 (a) indicating the % maximum and % reversible expansion for the first three pump cycles and (b) corresponding refractive index change.

Results and Discussion

Isomerization was induced in amorphous films of the azo copolymers by brief irradiation with the pump beam, and the corresponding change in film thickness was measured. The *trans*−*cis* conversion is depicted in Figure 2 as well as a schematic representation of the resulting photoexpansion response. As depicted, the isomerization of the initially *all-trans* state azo film leads to an initial irreversible expansion of the film when irradiated to the *cis*-rich photostationary state. Following the thermal *cis*−*trans* relaxation the film contracts, and upon further irradiation the film expands again, this time reversibly. A typical photoexpansion cycle profile of PDR1A is shown in Figures 3 and 4.

Upon irradiation for 30 s with circularly polarized light, an initial increase in film thickness of 3% was observed, with a corresponding decrease in refractive index, but this increase in thickness was not observed to be fully reversible on relaxation. Subsequent photoexpansion is reversible, however, as presented in Figure 4, along with the associated decrease in refractive index observed during the irradiation cycle. This refractive index decrease does not mirror the thickness increase exactly because the irradiated material now contains a mixture of *cis* and *trans* isomers which possess different refractive indices. The time scales required to reach saturation of the initial expansion are on the order of many tens of seconds to many tens of minutes depending on pump beam power. These time scales are significantly longer than the photochemically induced
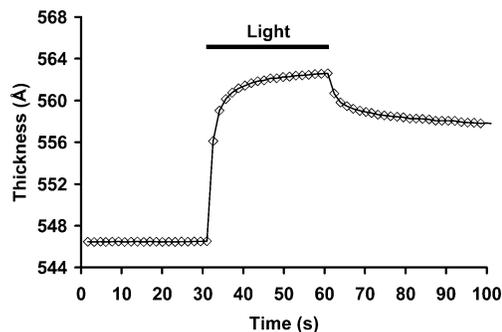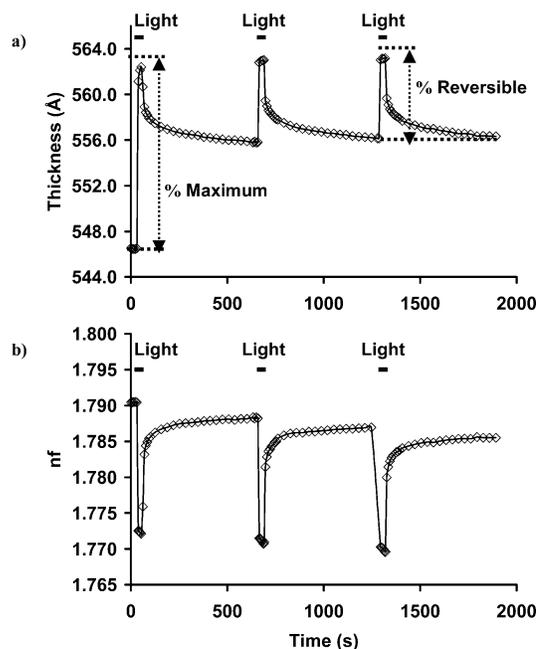
trans−*cis* isomerization of the azo polymer in pump-relaxation experiments which typically require under a few seconds to reach saturation. At low power, the expansion grows over time more slowly but eventually reaches the same extent of expansion obtained at high power. Since the saturation time depends on irradiation power, there is strong suggestion that it is the *trans*−*cis* cycling that drives the expansion of the film.

Azo isomerization alone has been shown to be on the order of microseconds or faster and has a high quantum yield, so in principle a brief irradiation of this time scale should be sufficient to cause expansion in the film. Irradiations of 1 s duration at a power of ~200 mW/cm^2 were observed to induce a measurable photomechanical response, though less than saturation, and the effect achieves more then 90% of its saturation of thickness change after 10 s of exposure. Although most of the characterization shown here used 30 s exposures to reach saturation, azo polymers exhibit sufficient response on shorter time scales to act as photoinduced actuators for some applications. Following a 10 min period where the azo polymer was allowed to thermally

relax with *cis−trans* thermal isomerization, the film was then irradiated again and expanded to an extent of 1.3% relative to the relaxation thickness. With repeated irradiation cycles, the extent of photoinduced expansion remained constant with a reversible expansion of ∼1.3%. During irradiation with circularly polarized light the dipoles of the azo moieties may tend to align in a direction perpendicular with the plane of the film which may induce some out-of-plane orientation, whereas in-plane orientation would be minimal since the incoming beam is circularly polarized. To ensure that upon isomerization the pump beam did not induce a significant orientation of the chromophores and hence the corresponding birefringence be misinterpreted as thickness change, studies were also conducted with an integrating sphere. This served to completely depolarize the pump beam as well as to make the beam nondirectional, and the same expansion profiles with refractive index conserved were observed. This indicated that the azo polymer chromophores remained unoriented when irradiated with circularly polarized light and thus did not interfere with ellipsometeric measurements, which assume an isotropic sample. Furthermore, birefringence was not observed in irradiated regions, measured through usual techniques.[9]

The initial nonreversible expansion of the film is due to a rapid *trans−cis* cycling that occurs during isomerization. Although 100 mol % PDR1A has a T_g of ∼95 °C, the rapid *trans−cis−trans* cycling likely also has a softening effect on the film, enhancing the photomechanical effect. Recently, Mechau et al. have shown a small change in the elasticity of an azo film due to a photoinduced mechanical softening effect.[28,29] The relatively long times required to reach maximum thickness imply that azo chromophores would undergo a large number of these *trans−cis−trans* cycles. It is proposed that this *trans−cis−trans* cycling requires an increase in the free volume of the polymer matrix because of the change in shape requirements between the *trans* and *cis* geometries, the local movement of the azo moieties, and the concomitant segmental motion of the polymer chains. These effects result in the observed increase in thickness and a reduction in the refractive index of the film, and when the pump beam was turned off, the film thermally relaxed as expected. The original film thickness, however, was not fully recovered after the first cycle, suggesting that the some of the photochemically induced free volume increase remains trapped in the polymer matrix. Similar findings were observed in azo-PMMA systems using a quartz crystal microbalance, where some of the free volume change induced by *trans−cis* isomerization was captured irreversibly in the film.[4] In our materials, however, when the film was heated above T_g in an attempt to recover the initial preirradiation film thickness, the resulting thickness after heating−cooling was 3.5% thinner than initial. This decrease in the irradiated film thickness above T_g may be due to a more efficient molecular packing achieved through the isomer cycling or also to the formation of density gradients in the film, as reported previously.[30−32] It is clear however that the thermal *cis−trans* relaxation alone is not as effective in repacking the polymer chains to their initial density as is heating the film above the glass transition temperature.

With repeated irradiation cycles the film expanded reversibly. After the first irradiation cycle, the free volume of the polymer matrix has reorganized and
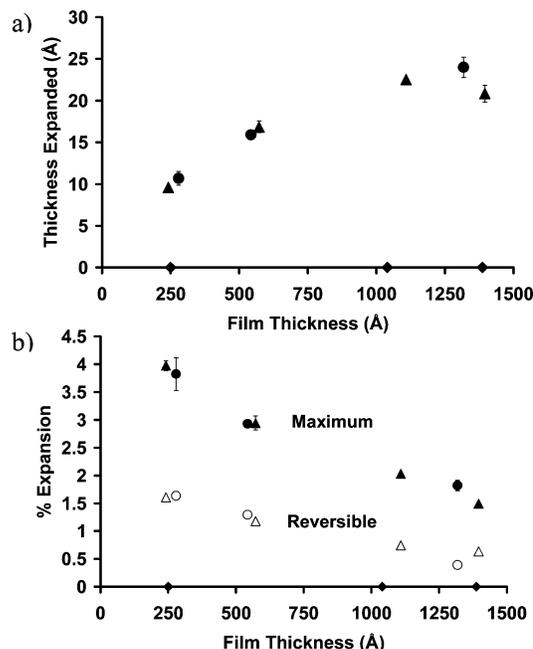

Figure 5. Thickness study for 100, 35, and 5 mol % copolymers irradiated at 514 nm (210 mW/cm^2). (a) The maximum extent of thickness increase obtained during irradiation, and (b) 30 s isomerization cycles following a 10 min relaxation showing % maximum and reversible expansion. The closed symbols ●, ▲, and ◆ correspond to the maximum expansion of the first cycle for 100, 35, and 5 mol % PDR1A, respectively. The open symbols correspond to the reversible expansion.

increased to its maximum, and the subsequent reversible expansion appears simply as an elastomeric response of the polymer matrix to light, through rapid *trans−cis−trans* cycling on irradiation. When the pump beam is turned off, the film undergoes *cis−trans* relaxation and the matrix deforms back reversibly. The time scale of this mechanical relaxation is at least an order of magnitude slower than the thermal *cis−trans* relaxation rate, suggesting that a slow material relaxation dominates after the chromophores have reverted back to the *trans* form in the dark. The relaxation profiles were fit to a first-order decay, and rate constants were found to be independent of the pump beam power, with a mean value of 0.006 ±0.001 s^{-1}, while typical *cis−trans* relaxation rate constants for PDR1A were measured to be ∼0.24 s^{-1}.[14] This would suggest that the reversible relaxation component is largely regulated by the polymer matrix and is not by the thermal relaxation of the *cis* fraction.

Similar photoexpansion measurements were then conducted varying the azo chromophore content of the polymer, the intensity of the pump beam, and the film thickness. The thickness dependence of PDR1A on the extent of expansion is shown in Figure 5. As depicted, the overall extent of thickness increase for the homopolymer and the 35 mol % copolymer is 10 Å in thin films (of ∼250 Å). As the film thickness is increased, the overall extent of expansion saturates at ∼23 Å in the thicker films in the range of ∼1200−1500 Å. The 5 mol % PDR1A showed no discernible change in film thickness when irradiated. The similar extent of expansion for the homopolymer and the 35 mol % PDR1A-*co*-AA as well as the zero extent of expansion of the 5 mol % PDR1A-*co*-AA can be attributed to the volume fraction of the azo moieties in the matrix. Even though the mole fractions appear quite different, the 35 mol %
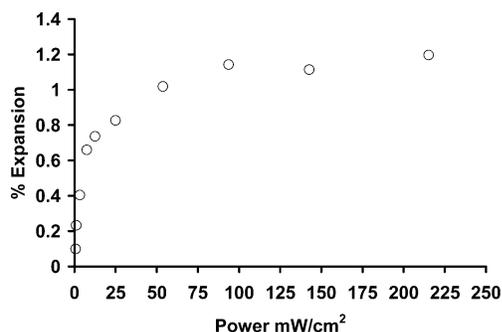
Figure 6. Pump laser power dependence on the extent of reversible expansion for a 220 Å, 100 mol % PDR1A irradiated at 514 nm.

PDR1A occupies a volume fraction of ∼70% azo in the material which provided a similar extent of expansion to that of the homopolymer, regardless of film thickness. However, the 5 mol % PDR1A copolymer has a volume fraction of only ∼20% and appears to be below a critical azo threshold to efficiently facilitate the movement of polymer backbone, and hence no thickness increase in the film was observed. This dependence on the azo content is nonlinear and suggests that a critical minimum concentration is required for a cooperative motion of the azo molecules to induce deformation of polymer matrix.

The homopolymer and the 35 mol % PDR1A-*co*-AA both exhibited a decrease in the extent of relative expansion as film thickness is increased for both the maximum (from 4 to 1.5%) and reversible components (from 1.5 to 0.5%), as shown in Figure 5b. The 100 and 35 mol % PDR1A-*co*-AA films both had a similar relative extent of expansion over the thickness range studied. The apparent decrease in the relative extent of expansion with increasing film thickness of the 100 and 35 mol % PDR1A-*co*-AA polymers is likely due to the extinction of the incoming pump beam near the free surface of the highly absorbing films. The molar absorptivity of the homopolymer was determined to be ∼4.3 μm^{-1} at 514 nm, which implies that for a film that is ∼1500 Å thick only ∼30% of the incident light will reach the substrate, whereas in a thin film of 250 Å more than 80% of the light will reach the bottom of the film. Therefore, thicker films expand to a lesser relative extent than thinner films due to a lower effective irradiation intensity near the substrate than at the exposed surface, which also implies that this observed expansion is in fact in the form of a gradient through the film, normal to the incident light.

The extent of reversible expansion of 100 mol % PDR1A vs the irradiation power is presented in Figure 6. At low pump beam power (0.7 mW/cm²) the film expanded to ∼0.1% reversible and saturated to ∼1.2% at ∼90 mW/cm². Above an irradiation intensity of ∼90 mW/cm² the extent of reversible photoexpansion appears constant. At low irradiation power, a measurable but smaller change in expansion can be induced, as the chromophores would be expected to suffer a reduction in the number of azo groups able to isomerize. This is due to the dominance of the thermal *cis*−*trans* conversion at low power, which reduces the *cis* population in the photostationary state and results in a low extent of expansion. At higher irradiation intensities the *trans*−*cis*−*trans* isomerization process would be expected to become more efficient, and hence the film expands to a greater extent, also as observed. Thus, the reversible

component can be attributed to the geometrical changes of the azo molecules during the irradiation and is dependent on the *cis* fraction in the film, whereas the irreversible expansion is dependent only on the *trans*−*cis*−*trans* cycling to induce a free volume change in the film. This behavior is comparable to that of the thickness dependence study, where a reduction in intensity occurs when the pump laser passes through the highly absorbing film.

This demonstration of a photomechanical effect that varies with irradiation intensity and azo content implies that this is a phenomenon general to all thin films of azobenzene polymers above a certain azo content. With a modest real expansion of just up to 4%, use as a light-driven actuator would require an amplification of the mechanical advantage for many applications, but there are many precedents already for similar materials, such as insect muscle systems which contract by only 2% yet can provide flight and piezoelectric materials which can function usefully with less than a 1% shape change. This study also suggests that previously observed light-induced mechanical changes (such as SRG formation) are probably due to this photomechanical effect, including a previously postulated rationalization of an isomerization pressure mechanism for SRG formation.[18,19] This proposed mechanism relies on the formation of a free volume pocket around the azo molecules, which results in a mechanical pressure exerted on neighboring polymer chains in regions of high light intensity. The pressure gradient that is formed by a corresponding interfering light gradient then drives plastic flow of the polymer to regions of low light intensity and requires only a few percent expansion with light for this to occur, similar to the range of the effect measured here directly.[19,20] The photomechanical effect could now be considered sufficient to drive a pressure-type mechanism in the formation of SRGs and other light-driven mechanical systems fashioned with azo polymers.

Conclusions

A photomechanical effect was observed in thin films of azo polymers, whereby light produces a reversible increase in thickness and a corresponding decrease in refractive index. The initial photoexpansion of PDR1A films is not fully reversible, but subsequent irradiation cycles exhibit a completely reversible expansion over many cycles. We have demonstrated that the relative extent of expansion of PDR1-*co*-AA copolymers can be controlled through film thickness and by varying the pump beam intensity or duration. The response of the polymer matrix appears to govern the relaxation rate of the polymers in the dark and not the thermal back-isomerization. Low power irradiation is sufficient in producing a photomechanical response in the azo films, and in principle these polymers could be developed as photoinduced actuators. This photomechanical effect appears to be of sufficient magnitude to explain some previously observed light-activated mechanical changes in similar materials, such as a pressure-type mechanism being responsible for the formation of SRGs in azo films.

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