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ARTICLE TYPE

Stimulating changes in the elastic modulus of polymer materials by molecular photochromism

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Photonastic materials are those that deform or change shape in a pre-determined or non-random fashion when exposed to light. We report here the elastic modulus of a photonastic polymer containing the photoreversible photochrome 10 [Ru(bpy)$_2$(pySO-NB)]$^{2+}$, where bpy is 2,2′-bipyridine, and pySO-NB is a chelating ligand containing a norbornene monomer attached through an amide group (Scheme 1), both pre- and post-irradiation. Nanoindentation results show that the polymer exhibits an increase in the elastic modulus (E) 15 upon irradiation. We propose a bilayer cantilever model to explain the macroscopic deformation. Our analysis reveals that the concentration of the ruthenium is an important parameter through the optical density of the film, the optical penetration depth and the force generated from irradiation.

20 Photonastic materials are those that deform or change shape in a pre-determined or non-random and repeatable fashion when exposed to light.[1] Such materials transduce light energy to mechanical energy and thus exhibit photomechanical properties. Nature provides a number of examples in the form of the opening 25 of flowers (e.g., tulips), or of an eye altering its focal length through muscular deformation of the lens.[2] Curiously, these examples operate on dramatically different timescales, and employ vastly different, yet equally complicated mechanisms. In plants, light initiates a cascade of reactions leading to differential 30 turgor (osmotic) pressures across cells, triggering the motive response; in vision, photoreceptors (retinal ganglion cells, rods and cones) induce electrical signals that lead to photoconstriction of the pupil. In these examples, a stress is applied, initiated by light resulting in a macroscopic bending of the material. The 35 Youngs' or elastic modulus of the material is an important parameter in understanding the amplitude of a deformation, as described by elastic bending theory.

Recently, a number of researchers have investigated crystals,[3-12] framework materials,[13-16] liquid crystals[17-23] and polymers[24-29] 40 that exhibit photonastic (photomechanical) behavior. Often, these materials comprise a photochromic unit that changes both electronic and molecular structure upon irradiation in a simple and reliable way. The analyses of these photonastic effects typically involve the differential volume in crystals, phase 45 changes in liquid crystals, and, in some cases, the mechanical properties of materials, but involve a summation of individual molecular changes in an ordered, regular environment as the

source of macroscopic shape change.[6, 10] We propose that disordered or amorphous materials containing a photochromic 50 solute or unit randomly oriented within the matrix might also demonstrate macroscopic shape change. A bilayer cantilever model could lead to bending if the optical density, optical penetration depth and generated strain (from the light applied stress) can be optimized for bending. Herein, we report the elastic 55 modulus of photonastic materials pre- and post-irradiation formed from polymers comprised of a photochromic monomer. The results show that the irradiated portion of the film hardens from isomerization, thus generating a concentration gradient (bilayer) and strain between the layers, which leads to bending in 60 disordered polymer films.

We previously reported the synthesis and basic photonastic response of our polymer containing the two-color reversible photochrome [Ru(bpy)$_2$(pySO-NB)]$^{2+}$, where bpy is 2,2′-bipyridine, and pySO-NB is a chelating ligand containing a 65 norbornene monomer attached through an amide group (Scheme 1).[24] Briefly, co-polymerization of norbornene (NB, m) with [Ru(bpy)$_2$(pySO-NB)](PF$_6$)$_2$ (n) leads to the production of polymers with varying ratios of m and n, dependent upon the reaction ratio in solution. The reaction mixture is then pipetted 70 directly into methanol solution inducing precipitation. The resultant colored polymer is re-constituted in dichloromethane solution, where it may be spin-coated or drop-casted onto a surface for further analysis or experimentation. Norbornene was chosen as the backbone polymer material because it exhibits a 75 low Tg, is readily polymerized and is transparent to visible light. Not addressed in the previous report was the affect of isomerization on the mechanical properties of the material.

Scheme 1. Co-polymerization of photochromic monomer with 80 norbornene.
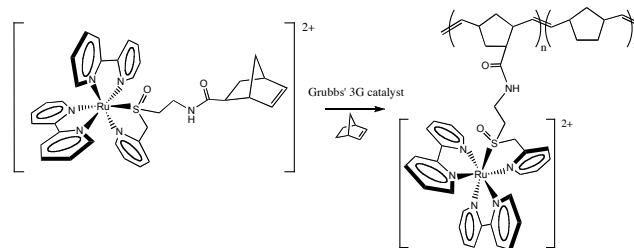
A summary of the photonastic properties of these polymers is

presented in the last column of Table 1 and a representative response is shown in Figure 1. Neither the poly-norbornene sample nor the poly-ruthenium thioether material (poly-[Ru(bpy)$_2$(pyS-NB)]/NB 1:40) show any macroscopic deformation when a 4.5 mm x 1.0 mm x 0.002 mm sample is irradiated with light absorbing in the MLCT (Metal-to-Ligand Charge Transfer) transition. This indicates that the polymer alone or a simple chromophore in the polymer that does not isomerize do not show any macroscopic changes upon exposure to light. However, the three poly-[Ru(bpy)$_2$(pySO-NB)/NB]$^{n+}$ samples, which differ in photochromic ruthenium loading, feature macroscopic deformation when irradiated within the MLCT absorption band. We found that the largest bending occurred for the 1:40 sample (1 Ru : 40 NB; Figure 1A,B) and smaller deformations occurred for the 1:25 and 1:150 samples (Table 1). Importantly, all three material samples show distinct color changes consistent with photoisomerization of the bound sulfoxide (S→O).[30] The bending of the polymer film can be reversed upon exposure to longer wavelength light ($\lambda > 450$ nm; not shown).[24] From molecular studies, this wavelength triggers O→S isomerization.[30] Thus, it is clear that photochromic isomerization occurs concomitant with macroscale deformation (bending). Changes in the properties of the material during isomerization that bridge these length scales are absent in our analysis.
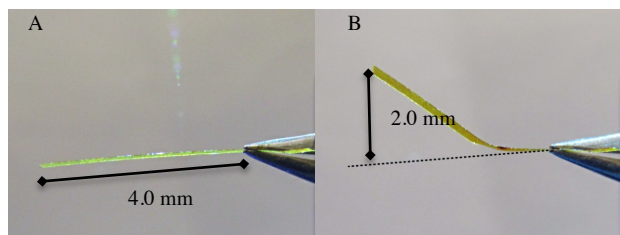

Figure 1. Digital images (side-on view) of a poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$ 1:40 copolymer film (A) prior to and (B) post irradiation with 405 nm light (100mW/cm^2). The dotted line in panel B represents the film-strip in panel A. The angle formed from the deformation is ~24 °.The 4.5 mm x 1.0 mm x 0.002 sample is formed via a drop-cast method from a concentrated dichloromethane solution onto Teflon. Evaporation of dichloromethane reveals a disc of poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$, which is readily removed from Teflon. A razor blade is employed to create uniform strips from the co-polymer disc. A single disc will provide 3 -5 such samples. Image J was employed to measure angle changes in the film post irradiation. The number of observed bending-unbending cycles is dependent on several factors such as sample preparation, residual solvent, and sample composition. For any sample, we observe no less than 5 and up to 30 bending-unbending cycles.

Relevant to bending, the Young's modulus or elastic modulus (E) of a material quantifies the stiffness of a material and is the ratio of applied stress to reversible strain along an axis; it is the linear slope of a stress-strain curve. A well-known procedure for determining the elastic modulus of a thin film is through application of the Oliver and Pharr model to results from nanoindentation experiments.[31] In this experiment, a cantilever of known dimension and mechanical properties impinges upon the surface. Mathematical treatment of the standard force-distance curves reveals the hardness, stiffness and elastic modulus of the material. We chose to employ this technique to measure this material property pre- and post-irradiation. We suspected that the isomerization must induce a change in the material in order for macroscopic bending to occur upon irradiation, given the relatively low concentration of the photochromic solute in the polymer.

Shown in Figure 2A is a digital AFM scan image of a film of poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$ 1:40 (ratio of Ru to NB monomer is 1:40) spin coated onto a glass cover slip. The white spots in the image are the remnants from individual nanoindentation experiments. In Figure 2B is shown a small area scan depicting the plastic deformation following an individual indentation experiment for poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$. The thickness of the film was determined to be ~3 μm by AFM. Since the penetration depth of the nanoindentation experiment is on the order of a few hundred nm, we conclude that there is no influence of the glass backing on the results of the nanoindentation experiment. Literature convention suggests that the indentation depth should not exceed 30% of the total film thickness; clearly, our measurements were performed within this threshold.[32]
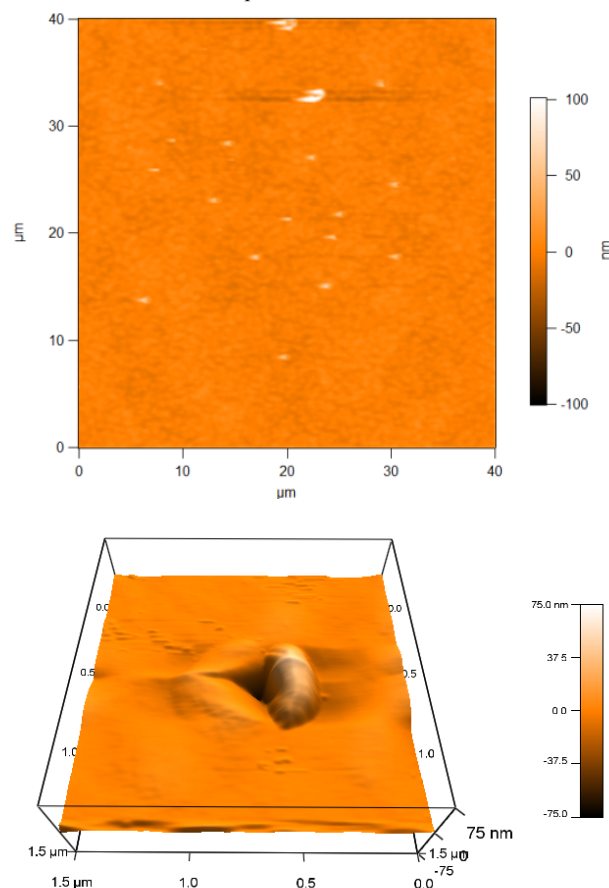

Figure 2. (A) Surface topology following nanoindentation for poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$ 1:40 copolymer film. The polymer is spin-coated onto a glass plate. (B) A small area scan highlighting a single indentation point.

Figure 3 shows the force vs indentation curves (unloading trace

only) obtained from these nanoindentation studies. In this plot, each color represents a different material and each trace represents an individual experiment. The different samples are poly-[Ru(bpy)$_2$(pySO-NB)/NB]$^{n+}$ 1:25 (black), poly-[Ru(bpy)$_2$(pySO-NB)/NB]$^{n+}$ 1:40 (orange), poly-[Ru(bpy)$_2$(pyS-NB)/NB]$^{n+}$ 1:40 (red), poly-[Ru(bpy)$_2$(pySO-NB)/NB]$^{n+}$ 1:150 (green) and polynorbornene (gray). A fit of each trace yields the stiffness, hardness and elastic modulus (See SI for the methodology). For polynorbornene, we obtain an elastic modulus or E_c of 140±11 MPa, a value that is in accord with literature values as determined from other techniques. Table 1 displays these data for all of the samples. In comparison of the different samples, it is clear that the incorporation of ruthenium within the polymer increases the elastic modulus, making the film more stiff or resistant to an impinging force. From the rule of mixtures for composite materials, this indicates that the elastic modulus for the ruthenium compound must be quite large given the low loading (1:40; ~ 2 mol % Ru).[33]
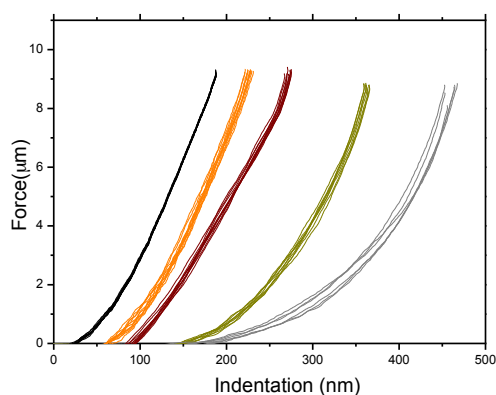

Figure 3. Force vs indentation curves for poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$ 1:25 (black lines), poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$ 1:40 (orange lines), poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$ 1:150 (green lines), poly-[Ru(bpy)$_2$(pyS-NB)/NB]$^{n+}$ 1:40 (brown lines) and poly-NB (gray lines).

We are interested in how irradiation of the photochromic polymer and subsequent isomerization yields changes in the mechanical properties of the polymer film. Accordingly, we irradiated (65mW/cm^2 405nm laser light for 60s) each of the film samples above and then re-performed the nanoindentation experiment. These data are presented in Table 1. Importantly, the elastic modulus does not change after irradiation of either the polynorbornene sample or the poly-[Ru(bpy)$_2$pyS-NB/NB]$^{n+}$ 1:40 sample. Polynorbornene is transparent to visible light and while the ruthenium-thioether sample does absorb light, the chromophore does not exhibit isomerization and should not induce a change in the mechanical properties. This latter observation is especially important because irradiation of this sample should induce local photothermal heating, which should not necessarily lead to a permanent change in the average elasticity of the film (clearly the elastic modulus changes *during* photothermal heating), but could lead to permanent photothermal deformations. In contrast, for the ruthenium sulfoxide photochromic polymer samples, a change in the mechanical properties of the film was observed following visible irradiation.

The greatest increase in the Young's modulus (from 503±16 to 713±19 MPa) is found for the sample with the largest and fastest deformation. These data demonstrate that irradiation of the polymer containing the ruthenium photochrome results in a substantial change in the elastic modulus of the film. We propose that it is this change that leads to macroscopic bending of the film.

The differences in E_c before and after irradiation for the poly-[Ru(bpy)$_2$(pySO-NB)/NB]$^{n+}$ 1:25 and poly-[Ru(bpy)$_2$(pySO-NB)/NB]$^{n+}$ 1:150 films deserve comment. For poly-[Ru(bpy)$_2$(pySO-NB)/NB]$^{n+}$ 1:150, we note a small but perceptible color change of the film (the film is nearly transparent at this low concentration), indicating isomerization following light irradiation. We suspect that the invariant elastic modulus (240±9 vs. 244±10 MPa) is due to the dilute concentration of the photochrome (it is still greater than pure polynorbornene). This is consistent with the absence of deformation in that a force great enough to bend the polymer is not generated upon irradiation. For poly-[Ru(bpy)$_2$pySO-NB/NB]$^{n+}$ 1:25, the small, but statistically significant increase (from 677±10 to 705±15 MPa) in the elastic modulus is caused by a reduced optical penetration depth (~400 nm) due to the greater concentration of the photochrome. Thus, the greater optical density of the film reduces the extent of conversion, generating a smaller force from irradiation, and a smaller photonastic effect. These data illustrate both the importance of the penetration depth and the optical density (concentration of photochrome) of the film. Clearly, the poly-[Ru(bpy)$_2$(pySO-NB)/NB]$^{n+}$ 1:40 sample exhibits an optimum balance of these factors.

We performed Gel Permeation Chromatography (GPC) experiments on the pre- and post-irradiated polymers to learn how the phototriggered isomerization affects the molecular volume of the polymer (hydrodynamic radius; radius of gyration) in solution (Table 1). We reasoned that if the molecular volume of the polymer is altered from irradiation (and isomerization), then this might help improve our understanding of the photonastic properties of these materials. Specifically, the hydrodynamic radius and the radius of gyration appear in the retention time of the polymer in this experiment, and reflect an apparent molecular weight. In accord with the AFM results above, neither poly-norbornene nor poly-[Ru(bpy)$_2$(pyS-NB)/NB] 1:40 (the ruthenium thioether polymer) show any change in the molecular weight distribution profile between pre- and post-irradiation samples. All three co-polymers containing the ruthenium photochrome exhibit differences in the molecular weight distribution profile following MLCT irradiation of the polymer in solution relative to the un-irradiated sample. For the 1:40 polymer, Mw (weight average molecular weight) and Mn (number average molecular weight) increase 17.7% (from 21870 to 25740) and 16.2% (7390 to 8587), respectively upon irradiation. Similarly, for the 1:150 polymer, Mw and Mn increase 12.8% (from 38150 to 43050) and 17.6% (12710 to 14950), respectively, upon irradiation. We also observed similar increases in Mw and Mn for the 1:25 polymer. It is important to note that irradiation should not actually increase (or otherwise change) the absolute molecular weight of the polymer, as the reaction is simply an isomerization. Thus, it is only certain that the hydrodynamic radius and radius of gyration of the solvated

polymer have been altered following irradiation. It is manifest from these data that photo-isomerization, even in polymers with low ruthenium concentrations, leads to changes in the 3-D structure of the polymer in solution and its interaction with the stationary phase pre- and post-irradiation. We suspect that certain of these structural changes are also operative in the polymer films, but the conformation changes generated upon isomerization will be different in solution than in the polymer film. Indeed, the friction in the solid medium is much greater than that in solution. We propose that these polymer conformation changes stimulate an increase in the elastic modulus of the polymer.

We are only aware of a few nanoindentation studies of polymers exhibiting a photonastic (photomechanical) effect. The most recent is from Priimagi and Barrett and co-workers on azobenzene-containing materials.[34] In aggregate, both the structural nature of the polymer and the energy and polarity of the light (visible vs. UV) are shown to affect on whether the polymer hardens or softens upon irradiation.[34] For visible light irradiation, which triggers *trans-cis-trans* cycling, the polymer always softens exhibiting a *decrease* in the elastic modulus, no matter the degree of cross-linking or other microstructural details.[34, 35] An increase in the modulus is only observed for UV irradiation (trans-cis isomerization; no cycling) of azobenzene doped polymer or when functionalized within a side-chain.[36, 37] Interestingly, Priimagi and Barrett conclude from their studies that the photosoftening effect is determined in part by the strain rate, with larger rates leading to greater softening. While it is tempting to make comparisons between our work and that of azobenzene polymers, a primary, critical distinction between the samples is difference in chromophore concentration. Our samples feature a ratio of 1:40 (Ru:norbornene), whereas the ratio of azobenzene to monomer is typically on the order of 1:2. At present, our polymer synthetic strategy does not permit this level of incorporation of Ru monomer, we are re-designing the polymer in order to reach these concentrations.

These data permit the formation of the bilayer cantilever model in a disordered system, which comprise the critical parameters of optical penetration depth, thickness of the sample, and force generated from irradiation. Shown in Figure 4 is a depiction of the sequence of events leading to bending. The top image represents a side-on view of the polymer film prior to irradiation. Following irradiation, the photochromes nearest the light source isomerize. The depth of isomerization is due to the concentration of the photochromic compound within the material. Consistent with the GPC data, isomerization induces a change in the local polymer conformation, leading to macroscopic contraction in the film. The isomerized portion of the film undergoes an increase in the elastic modulus and stiffness of the film. We speculate that the conformation change is a local hardening, with the polymer chain moving into void spaces. Thus, density is not conserved. The stiff side of the film acts upon the soft, back half of the film to produce macroscopic bending. In this mechanism, photonic energy is transduced to potential energy for excited state bond breaking and bond forming reactions. Isomerization induces a change in the 3-D structure of the film, ultimately producing bending. This model readily explains why bending may not be observed in materials with too great or too low an optical density.

In the former case, the portion of the irradiated film is too thin to generate a large enough force for bending, while in the latter case, the generated force is too small since not enough light is absorbed. This mechanism also explains the attenuation of bending that we observe upon repeated exposure to light. The polymer film upon irradiation moves into a void space. Upon re-irradiation at a longer wavelength, the O→S isomerization is reversed. However, the motion of appended polymer chain is not the microscopic reverse of the forward isomerization and thus the exact structure prior to irradiation is not attained. Upon repeated cycles, there is no longer accessible void space and the polymer ceases to bend.
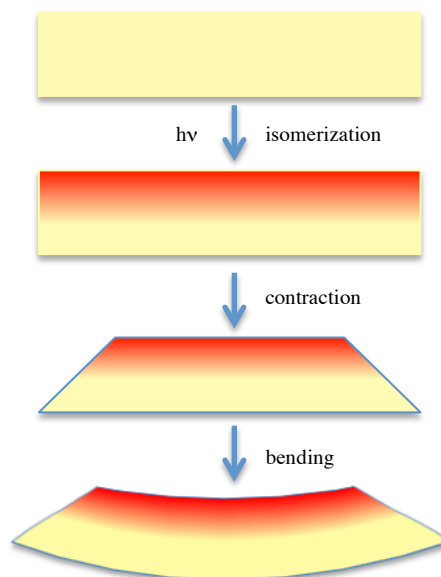

Figure 4. Proposed mechanism for macroscopic bending in disordered photochromic polymer materials. From a side-view perspective, irradiation of the polymer sample containing photochromic ruthenium sulfoxide triggers isomerization and a color change of the sample. Isomerization leads to hardening of the sample, a loss of volume for the irradiated area, and a contraction of film. This contraction bends the macroscopic sample.

Conclusions

We have demonstrated how a photochromic compound can stimulate large macroscopic shape change in a material at low concentrations and in a disordered or amorphous environment. The critical parameters are the optical penetration depth, the optical density of the film and the force generated upon irradiation. The salient point is that large bending deformations in samples containing a relatively small concentration of chromophore is observed. This is in contrast to many existing crystalline, co-crystalline and azobenzene polymers where the chromophoric concentration is much greater. In conjunction with other studies, these data will help to establish an overall hypothesis for bending in photonastic polymers and materials.

Notes and references

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Table 1. Elastic (Young's) Modulus, Molecular Weight and Bending Angle for polynorbornene polymers before and after irradiation.

Name		E_c (MPa)	Mw	Mn	PDI	Bending Angle[a]
poly-NB	Pre-Irr.	140±11	101,600	27,030	3.76	0°
	Post-Irr.	133±11	101,600	27,030	3.76	
poly-RupySO-NB /NB 1:25	Pre-Irr.	677±10	25190	12080	2.09	20°
	Post-Irr.	705±15	29570	12820	2.31	
poly-RupySO-NB /NB 1:40	Pre-Irr.	503±16	21,870	7,390	2.96	39°
	Post-Irr.	713±19	25,740	8,587	3.00	
poly-RupySO-NB /NB 1:150	Pre-Irr.	240±9	38,150	12,710	3.00	0°
	Post-Irr.	244±10	43,050	14,950	2.88	
poly-RupyS-NB /NB 1:40	Pre-Irr.	336±9	24,660	8,715	2.83	0°
	Post-Irr.	318±9	24,660	8,715	2.83	

a. The bending angles were obtained from films with dimensions of 4.0mm x 1.0mm x 0.002mm.

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