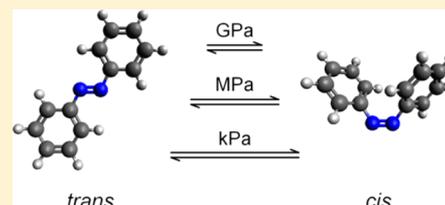


Azobenzene Photoisomerization under High External Pressures: Testing the Strength of a Light-Activated Molecular Muscle

Thomas A. Singleton,[†] Kevin S. Ramsay,[†] Mirela M. Barsan,[†] Ian S. Butler,[†] and Christopher J. Barrett^{*†}[†]Department of Chemistry, McGill University, Montreal, Quebec H3A 0B8, Canada

ABSTRACT: The photoinduced isomerization and thermal back relaxation of an azobenzene-functionalized polymer poly(disperse red 1 acrylate) were investigated at increasing external pressures up to 1.5 GPa inside a diamond-anvil spectroscopic cell. The thermal *cis*–*trans* isomerization was monitored by laser pump–probe spectroscopy, which demonstrated an increase in the half-life of the isomerization process with increasing pressure. Additionally, the *cis* content of the photostationary state gradually decreased as a function of pressure, with complete arrest of the *trans*–*cis* photoisomerization above 1.5 GPa. The fact that the photoswitching behavior however could still be observed beyond 1 GPa is remarkable and is effectively a measure of the strength of the azobenzene chromophore as an artificial muscle. The changes in the Raman shifts of both *trans*- and *cis*-azobenzene were also investigated from ambient pressure up to 4 GPa, and no discontinuities were observed in the pressure vs wavenumber plots indicating no change in phase. The *cis*–*trans* photoisomerization of azobenzene was shown however to still be inducible at all the pressures investigated, confirming the suitability of these molecules for high-efficiency light actuation.



INTRODUCTION

At the heart of all members of the large family of azo-aromatic chromophores is the parent azobenzene molecule, which consists of two benzene rings joined by an N=N double bond. These molecules are ubiquitous in everyday life, forming the core of more than 70% of commercial dyes owing to their vibrant, chemically tunable colors, and extreme durability even upon continuous irradiation.^{1,2} Most recently, azo compounds have also been the subject of numerous photoswitching studies by the chemistry, physics, and engineering communities because of their wide-ranging photochemical and photophysical properties. Upon irradiation with a suitable wavelength of light (in the UV or visible), a change from the stable *trans* isomer to the metastable *cis* isomer is induced, a process which can be reversed either photochemically or thermally. This reversible geometric effect was first noted in 1937 by Hartley, when he observed that the solubility of azobenzene changed upon irradiation.³ Except for some special cases where isomerization is extremely sterically hindered,^{4,5} essentially all azobenzene derivatives are capable of undergoing this reversible *cis*–*trans* photoisomerization (Figure 1 a).

Although influenced somewhat by the electronic and steric effects of particular derivatives, the same basic geometry is present in most azo-containing molecules.⁶ Of most recent interest, in addition to the microscopic change in molecular structure, isomerization has now been developed to induce large-scale secondary effects in polymers and materials containing azo chromophores. These effects vary in size scale and magnitude, ranging from the molecular length scale as light power for molecular machines,^{7–9} through to macroscopic formation of micrometer-sized surface patterns upon irradiation,^{10,11} and even deformation of coated substrates to transfer mechanical work as layers of “artificial muscles” actuating over many centimeters.^{12,13} Despite these many recent applications

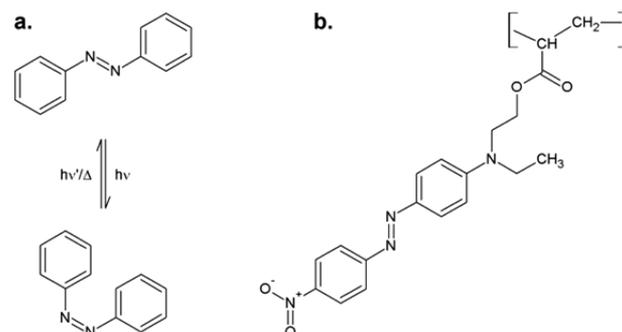


Figure 1. Two azobenzene chromophores investigated in this study: (a) *trans*-(*E*)-azobenzene, on the top left, adopts a planar geometry, while the benzene rings on *cis*-(*Z*)-azobenzene are skewed out of plane;¹⁴ (b) PDR1A, on the right, consists of the disperse red 1 chromophore bound to a polymeric acrylate backbone.

however, there remains great uncertainty over the basic mechanism of photomechanics, and even the isomerization itself, and the limits of how much light energy can be harvested and transduced. Until there is a far more complete set of basic physical measurements into the effect, materials cannot be optimized for any of these applications.

In this pressure study, we examined both the simple parent molecule azobenzene and one of the most successful photoswitch derivatives, poly(disperse red 1 acrylate) (PDR1A; structure depicted in Figure 1 b), based on the disperse red 1 azo dye. The simple parent azobenzene molecule receives less attention in recent material applications but is well suited for fundamental studies into its isomerization mecha-

Received: June 20, 2012

Published: July 16, 2012

nism, and due to its structural simplicity is valuable as a starting point for new spectroscopic techniques. Azobenzene also exhibits a very slow thermal *cis*–*trans* reconversion rate relative to most functionalized derivatives, allowing the most facile investigation of the *cis* form by Raman spectroscopy under pressure at ambient temperature conditions, since these experiments require samples to be stable for hours. PDR1A is a more recent azo derivative polymer material that was developed in the 1990s and widely applied to optic, photonic, and holographic applications owing to its fast switching, photorefractivity, photoreorientation, and stability as a data-storage medium. It was developed to optimize optical properties and speed and efficiency of photoswitching, necessary for the transmission-based kinetics measurements reported here: thermal reconversion rates are on the order of seconds. This allows for a substantial amount of kinetic data to be acquired in a relatively short time frame without requiring the use of ultrafast laser equipment. The absorption spectrum of PDR1A is also amenable to pump–probe kinetic measurements at convenient and noninterfering wavelengths in the visible—the peak absorbance is a broad feature at approximately 480 nm in the solid phase—making the choice of pump and probe wavelengths straightforward and not requiring the added complication of UV light sources.

Mass surface migration of azo thin films upon irradiation with isomerizing wavelengths of light is another fascinating and curious effect unique to azo-functionalized materials.^{15–19} Pressure has been implicated as the leading mechanism by which repeated isomerization could induce macroscopic movement of the material, yet more fundamental studies are needed.^{20,21} The free volume requirement for isomerization to proceed is larger than the volume of either the *trans*- or *cis*-azo chromophore,^{22–24} and thus isomerization occurring in free volume pockets in the host material smaller than this isomerization requirement can generate a local pressure. A chromophore birefringence study of the effect of pressure up to 0.2 GPa on information storage ability in an azo-doped polymer was reported by Sekkat et al., who noted a retardation in the rate of orientation at these moderate pressures: another study by this group also suggested the onset of isomerization hindrance in this modest pressure regime.^{25,26} We report here the results of a full high-pressure visible and Raman spectroscopic study of the basic process (up to 4 GPa) of the thermal and photoinduced *cis*–*trans* isomerization of the azobenzene molecule, as well as an examination of the kinetics of the *cis*–*trans* thermal isomerization of PDR1A under pressure.

EXPERIMENTAL SECTION

Raman Measurements. Raman spectra were obtained using an inVia Renishaw spectrometer equipped with a CCD detector and two laser sources (514 nm visible Ar⁺ ion and 785 nm NIR diode). Measurements made using the 514 nm laser (Spectra-Physics) involved a 2400 line/mm diffraction grating and a holographic notch filter, while for the 785 nm laser (Renishaw), a 1200 line/mm diffraction grating and an edge filter were employed. In order to achieve the best possible resolution while avoiding damage to the sample, the power of the 514 and 785 nm lasers was varied in the ranges of 0.15–1.5 and 3–30 mW, respectively. The Raman spectrometer was calibrated prior to each set of measurements by exciting a silicon sample placed under the microscope and performing an automatic offset correction. The proprietary Renishaw WiRE

2.0 software was used for the data acquisition and subsequent treatment.²⁷ All measurements were performed at room temperature, and the experimental data are considered to be accurate to within ± 1 cm⁻¹.

High-Pressure Apparatus. The high-pressure measurements were carried out in a diamond-anvil cell (DAC), furnished by High Pressure Diamond Optics, Tucson, AZ and fitted with type-IIA diamonds. Samples were introduced, together with several ruby chips, into the 300 μ m circular hole of a stainless-steel gasket (7 mm \times 7 mm \times 270 μ m) and squeezed between the parallel faces of the DAC. The change in fluorescence wavelength of the R₁ line (²E \rightarrow ⁴A₂) of ruby was used to determine the applied pressure.²⁸ The DAC was mounted on the XYZ manual stage of a Leica microscope, and the laser beam was focused onto the sample through a long-working-distance 20 \times objective. No pressure-transmitting medium was used for solid azobenzene samples; glycerol was used for the kinetic measurements of the PDR1A isomerization. After each increase in pressure, the sample was allowed to equilibrate for a minimum of 20 min prior to data collection.

Kinetic Measurements. The thermal *cis*–*trans* isomerization of PDR1A films was measured at various pressures between ambient and 4 GPa using the diamond-anvil cell. A thin film of the polymeric chromophore was deposited on one face of the diamond-anvil cell by placing a drop of concentrated solution of PDR1A in tetrahydrofuran (Fisher Scientific, HPLC grade) on the face of one diamond anvil and allowing the solvent to evaporate. Owing to the thermally sensitive nature of the apparatus, the films were not annealed, so some residual solvent likely remained in the film thus lowering the bulk modulus. The optical density of the films investigated varied between approximately 1.3 and 1.5 at 488 nm. The films were inspected for optical clarity, and then the DAC was assembled as described in the previous section. Pump–probe *trans*–*cis* flash photolysis kinetic measurements at various pressures were acquired using the optical apparatus shown in Figure 2. *Trans*–

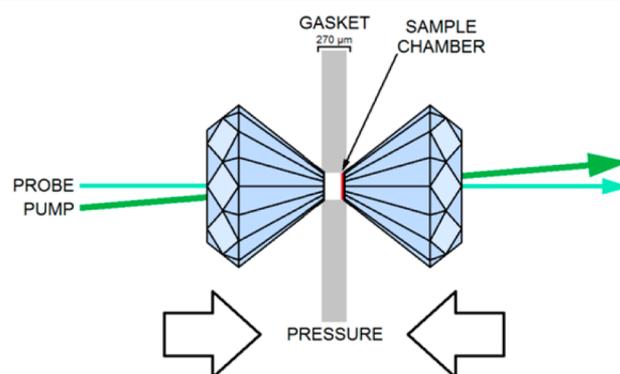


Figure 2. Pump–probe beam geometry through the diamond-anvil cell. A film of PDR1A approximately 1 μ m thick is held in a 270 μ m thick gasket between the two diamond faces. The void volume of the gasket (300 μ m diameter) is filled with glycerol to act as a pressure-transmitting medium.

cis photochemical isomerization was induced in the film by irradiation with a 100 mW·cm⁻² circularly polarized, unfocused beam from a frequency-doubled Nd:YAG laser operating at 532 nm. Circular polarization was used to avoid orientation of the azobenzene chromophores, which could result in anisotropic absorbance readings.²⁵ Typically, a pump cycle of between 0.5 and 1 s was used to induce isomerization and ensure saturation

of *cis* isomer in the photostationary state; this period of irradiation at $100 \text{ mW}\cdot\text{cm}^{-2}$ was low enough to avoid heating the sample, so the kinetic measurements can be considered acquired at room temperature.²⁹ A 488 nm probe beam from an argon ion laser was chopped mechanically at 1410 Hz and attenuated to $<1 \mu\text{W}$ and then passed through the sample to a photodiode detector, where the intensity was recorded as a function of time. The intensity of the probe beam is proportional to the *cis* content of the film and can be converted to an approximate fraction of the film isomerized to the *cis* isomer using the molar absorptivity values for *cis* and *trans*-PDR1A from ref 30.

Sample Preparation. *trans*-Azobenzene (tAB) was purchased from Sigma-Aldrich ($\geq 99\%$ purity by HPLC) and was used without further purification. *cis*-Azobenzene (cAB) was prepared by adaptations of the method used by Cook and the observations of Frankel and Wolovsky.^{31,32} A concentrated solution of tAB in light petroleum ether was irradiated at 365 nm with a Driel 200W mercury–xenon UV lamp for 16 h at 23 °C in order to generate cAB. The cAB was then separated from the tAB on a 20 cm silica column by eluting the mixture with light petroleum ether. The cAB was visible as a dark orange band that was retained in the top 5 cm of the column, while the tAB was eluted by the petroleum ether. After all visible remnants of the tAB had been removed, the cAB was eluted with acetone and collected. The cAB was then dried by rotary evaporation in an ice bath (to prevent thermal conversion to tAB) followed by vacuum filtration at room temperature in a dark environment. The cAB was stored in the dark at $-15 \text{ }^\circ\text{C}$. Before the Raman spectra were collected, the purity was checked by thin layer chromatography (TLC), and there was no evidence of tAB.³³

The effect of external pressure on the kinetics of the thermal *cis*–*trans* isomerization was investigated using a low-molecular-weight polymer of disperse red 1 acrylate, purchased from Sigma-Aldrich (T_g 79 °C) and used without further purification.

RESULTS AND DISCUSSION

Poly(disperse red 1 acrylate). A typical pump–probe curve for PDR1A is presented in Figure 3. The ordinate value is the *cis* composition of the sample expressed in mole percent, calculated from the optical density of the sample using

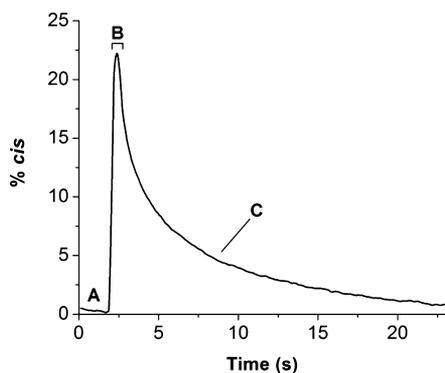


Figure 3. Typical pump–probe curve of a PDR1A in the diamond anvil-cell. The plot can be broken into three sections: (A) the initial all-*trans* state with pump light off, followed by (B) pump light on where the sample quickly reaches its photostationary state, and finally (C) thermal relaxation of the *cis*-PDR1A chromophores after the pump light is turned off.

absorptivity values derived from ref 30. The absorptivity value employed here, for a poly(methyl methacrylate) (PMMA) film doped with nonpolymeric disperse red 1 (DR1), should have similar enough optical properties to the PDR1A samples investigated to approximate the composition of the sample as a function of time. For an arbitrary film an all-*trans* DR1-PMMA sample will have an optical density of 0.65, while the same film with all chromophores in the *cis* form will have an optical density of 0.35. The absorbance of the sample at any time for any composition can be written as

$$A_t = A_{cis} + A_{trans} \quad (1)$$

And, expressing each absorbance as a product of the absorptivity and mole fraction

$$A_t = \alpha_{cis}f_{cis} + \alpha_{trans}f_{trans} \quad (2)$$

This expression can now be converted to an expression containing only the fraction of the sample in the *cis* state, using the relation

$$f_{trans} + f_{cis} = 1 \quad (3)$$

Inputting all the known values gives an expression for the *cis* fraction, normalized to $A_{trans} = 1$

$$f_{cis} = \frac{1 - A_t}{0.46} \quad (4)$$

This value is then multiplied by 100% to yield the percentage of the sample in the *cis* form.

The pump power necessary to achieve the highest possible *cis* conversion was determined by varying the pump power at ambient pressure until no further decrease in absorption intensity was observed; this situation was also verified periodically at elevated pressures to ensure this value did not change. The effective pump power required was determined by the photochemical quantum yields of the *cis* and *trans* isomers of the azobenzene chromophore, and these values could be determined by the method developed by Sekkat et al.³⁰ A pump intensity of $100 \text{ mW}\cdot\text{cm}^{-2}$ was found to be adequate to achieve this level of conversion, which is typical for azobenzene samples in the literature. This power has also been shown to be low enough to not cause permanent burn damage to the sample.³⁴

The averages of several of these curves at a given pressure were plotted as $\ln[A_\infty - A_t]$ versus time, where A_∞ represents the all-*trans* absorptivity at “infinite time,” yielding an approximately linear plot with a slope of $-k$. The data from the first few seconds after the pump beam was shut off were omitted from the analysis, as deviation from linear kinetics was observed in these samples. When this brief anomalous region is omitted, rate analysis is cleanly first-order, as per usual data treatment in the solid state.^{22,35}

Figure 4 illustrates the decrease in the *cis* chromophore population in the photostationary state as the external pressure on the sample was increased. In the previous study by Sekkat et al. discussed previously,²⁵ it was found that the free volume of azo-functionalized polymer films exposed to high external pressure decreases, thereby affecting the rate of photo-orientation of the chromophores when exposed to polarized light. These authors found that the extent of chromophores able to reorient within the polymer decreased linearly with applied pressure from ambient up to 0.15 GPa, along with an associated pressure dependence of the thermal *cis*–*trans* isomerization rate. That observation appears consistent with

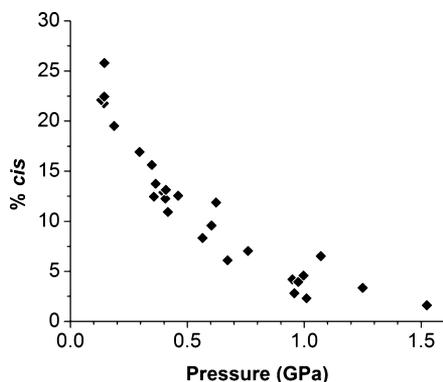


Figure 4. Plot of the fraction of *cis* in the photostationary state upon being irradiated by 532 nm light under high external pressure.

our measurements, which cover a pressure range an order of magnitude greater than the data in ref 25. It was suggested that their results are consistent with a model of motion retarded by molecular friction—the matrix surrounding the chromophores hinders the motion of the chromophore while it sweeps out a relatively large volume during isomerization. Interestingly, the molecular orientation effect investigated in ref 25 is quenched at 0.15 GPa. It seems clear that reorientation of the entire chromophore to align the dipole with polarized light, along with the covalently attached polymer backbone, has a much higher free volume requirement than does simple *trans*–*cis* isomerization without orientation. This lends further credence to decreased free volume in the film resulting in increased molecular friction.

The rate of isomerization of PDR1A showed an increase in half-life by an order of magnitude over the range of pressures investigated, before the photochemical process that generates the *cis* isomer is ultimately shut down (Figure 5). First-order

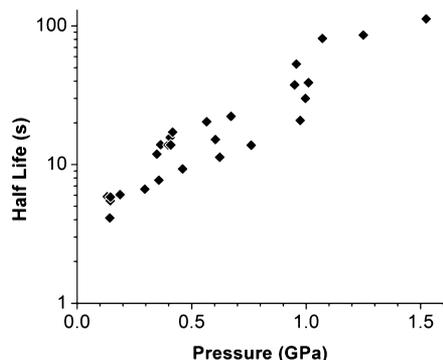


Figure 5. Plot of first-order half-life of the thermal *cis*–*trans* isomerization in PDR1A as a function of external pressure.

kinetic processes are not dependent on the initial concentration of reactants, and it has been shown repeatedly in the literature that repeated pump cycles on typical chromophores have no effect on the kinetics of the process.³⁴ This indicates that the retardation of the isomerization is purely an effect of the external pressure. As with the fraction of the sample able to undergo isomerization, discussed above, the decrease in film free volume and corresponding increase in molecular friction appear to hinder the thermal *cis*–*trans* isomerization event, resulting in the observed increase in thermal half-life.

***trans*-Azobenzene.** It is well-known that applying an external pressure to a crystal leads to a compression of the unit

cell, an amplification of interatomic and intermolecular interactions, and an increase of the energy of the vibrational modes.^{36,37} Solid *tAB*, at atmospheric pressure, takes up 0.4% less volume than does *cAB* due to differences in the crystal packing order of the molecule.⁶ In solution, calculations have shown that the free volume required for isomerization is 0.12 nm³ for inversion or 0.25 nm³ for rotation,²² but, to our knowledge, no consideration of the volume for solid isomerization has been undertaken. Given the previously mentioned volume considerations and the energy gap between the two isomers (49.1 kJ·mol⁻¹),³⁸ it would not be expected that mechanical pressure could force isomerization from *tAB* to *cAB*, because although the molecular volumes of the *trans* and *cis* isomers are similar, the volume of the transition state required to convert between them is significantly larger.²⁰

Successive measurements were made at increasing pressures up to 4 GPa using a 514 nm probe laser. Plots of wavenumber versus pressure were linear suggesting that no phase transition occurred up to 4 GPa (Figure 6). The associated dv/dP values

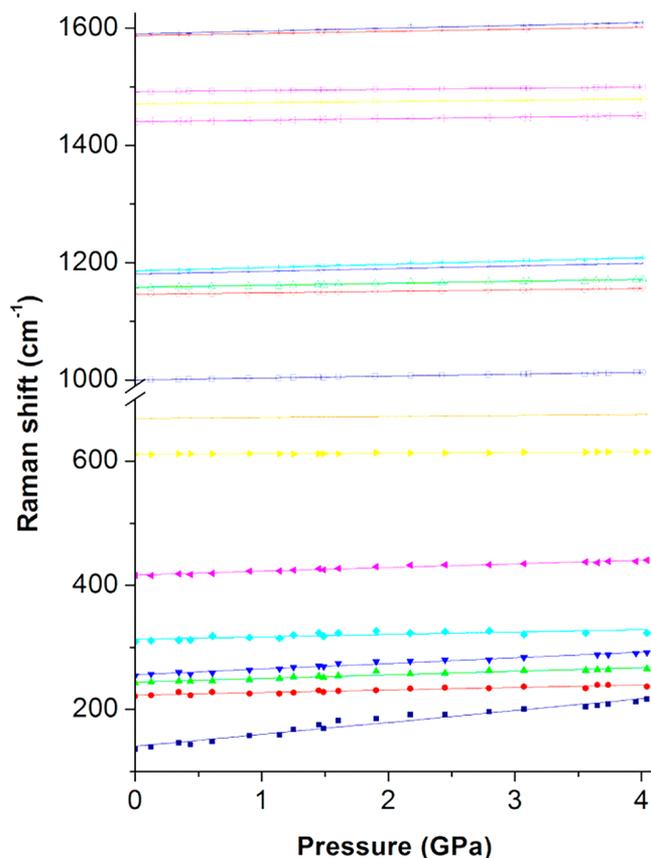


Figure 6. Pressure dependences of the principal Raman wavenumbers of *tAB*.

for *tAB* vibration are listed in Table 1. No peaks were formed that would correspond to *cAB* (as determined by comparison with spectral acquisitions for *cAB* at atmospheric and high pressure with a 785 nm laser), so it was determined that *tAB* was not being isomerized to *cAB* by the applied pressure. The peak that was initially present at 1588.9 cm⁻¹ split into two peaks. It was observed that several new peaks between 1400 and 1700 cm⁻¹ started to appear at a pressure of ~0.6 GPa, and they were persistent until a pressure of ~3 GPa. However, it is felt that these few spectral changes cannot be attributed to an

Table 1. Pressure Dependences of tAB Raman Peaks

wavenumber (cm ⁻¹)	dν/dP (cm ⁻¹ /GPa)
136 (135)	19.1 (9.8)
221	4.4
243 (243)	5.8 (5.6)
254	9.0
415	5.9
613 (605)	0.8 (0.8)
668	1.4
1000 (998)	3.2 (2.8)
1145 (1142)	2.4 (3.7)
1158 (1156)	3.5 (4.9)
1180 (1182)	4.6 (4.5)
1185	5.5
1440	2.2
1471	1.8
1491 (1483)	1.8 (2.2)
1586	3.6
1590 (1590)	4.5 (3.1)

actual phase transition, and some related high-pressure work on azobenzene and hydrazobenzene that has recently been reported by Song's group supports this contention.³⁹ In their study, the two compounds were also compressed in a DAC at room temperature, but up to much higher pressures of 28 GPa, followed by subsequent decompression. *trans*-Azobenzene did undergo a phase transition but at about 10 GPa, and further compression to 18 GPa resulted in an irreversible breakdown of the molecular structure. Some band positions and dν/dP values were also reported, and a few of these data are compared in Table 1 (in parentheses). The proposed vibrational assignments based upon their *ab initio* calculations are also reported in their paper. The pressures dependences are for the most part in reasonable agreement with one another.

***cis*-Azobenzene.** The Raman spectrum of a sample of cAB collected using the 514 nm laser shows only the features characteristic of tAB, indicating that cAB converts to tAB on exposure to light of this wavelength. However, when the 785 nm laser was used the Raman spectra of the two isomers were distinct.

Figure 7 shows the Raman spectra of a sample of cAB measured in the same spot using the following sequence of excitations lines: 785, 514, and 785 nm. The peak at 1511 cm⁻¹,

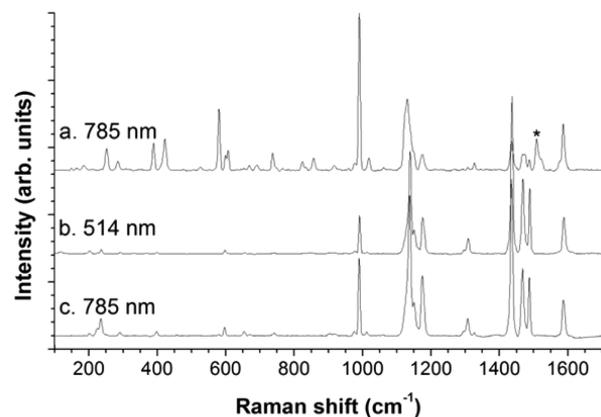


Figure 7. Raman spectra of a sample of cAB measured in the same spot with the following sequence of excitation: (a) 785 nm; (b) 514 nm; (c) 785 nm.

assigned to N=N stretching vibration of cAB, is only present in the first Raman spectrum measured with the 785 nm laser.⁴⁰ After the sample was exposed to the 514 nm laser, which produced a tAB spectrum, the 785 nm laser also produced a spectrum corresponding to that of tAB. This result was clearly due to photoisomerization occurring when the sample was exposed to the 514 nm excitation. Furthermore, it was found that the area of the cAB isomerized by the 514 nm laser was limited to that part of the sample where the beam had been focused, while the scattered light did not affect the cAB in the area adjacent to the laser beam.

Up to a pressure of ~3.2 GPa, the Raman spectra from a sample of cAB, collected with the 514 nm laser, still showed features only characteristic to tAB leading to the conclusion that mechanical pressure cannot lock the *cis* form into a stable enough configuration so that photoisomerization is prevented. Spectra collected from region 5 of a cAB sample with a 785 nm laser—both at high pressure and after the pressure was released—still produced the *cis* spectra and therefore showed that mechanical pressure (up to 3.2 GPa) cannot force isomerization of cAB to tAB. This result shows that photoisomerization can occur not just in solids but even in solids under high pressures.^{41,42} Furthermore, the spectra of the azobenzene at atmospheric pressure after being photoisomerized at high pressure is that of pure tAB suggesting that the isomerization occurs just as cleanly (without side reactions) and reversibly as it does in solution at atmospheric pressure.

CONCLUSIONS

The *trans*–*cis* photoisomerization and *cis*–*trans* thermal isomerization of poly(disperse red 1 acrylate) was investigated over a large range of external pressures. It was found that the fraction of the film that could be photoisomerized to the metastable *cis* form decreased from over 25% at ambient pressure to less than a detectable amount above 1.5 GPa. This indicates a reduction in free volume in the film, which reduces the number of chromophores able to undergo photoisomerization from the *trans* to the *cis* isomer. In addition, the half-life of the thermal *cis*–*trans* reverse reaction increased by an order of magnitude, showing high pressure diminished significantly the rate of isomerization as well as the extent of the isomerization. The effect of high pressure on the Raman spectrum of tAB has been investigated at room temperature with the aid of a DAC up to 4 GPa. All the Raman modes of tAB were shifted linearly toward higher wavenumbers with increasing pressure, indicating no phase transition occurred in this pressure range. In addition, it was found that external pressure up to 4.1 GPa cannot force the isomerization of tAB to cAB. Up to 3.2 GPa, cAB is photoisomerized to tAB, when irradiated with 514 nm light, as shown by the disappearance of the N=N stretching mode at 1511 cm⁻¹.

Taken together these studies demonstrate the robustness and effectiveness of the azo chromophores under extreme pressures over many isomerization cycles. The fact that reversible photoswitching could be induced in PDR1A even at more than 1 GPa (albeit somewhat diminished compared to atmospheric pressure) also demonstrates convincingly that the azo molecules have the capacity to be employed as quite powerful molecular muscles. This is also a clear demonstration of harvesting photons of sunlight wavelength and intensity to perform a considerable amount of mechanical work; thus, these azo materials can be regarded as promising for solar light

transducing materials, directly from light energy to mechanical work, robustly, reversibly, and efficiently.

AUTHOR INFORMATION

Corresponding Author

*Phone: (514) 398-6919. Fax: (514) 398-3797. E-mail: christopher.barrett@mcgill.ca.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for funding to NSERC Canada, the Canadian Foundation for Innovation (CFI) infrastructure and equipment grants, and to Professor Mark Andrews for helpful discussions.

REFERENCES

- (1) Zollinger, H. *Azo and Diazo Chemistry*; Interscience: New York, 1961.
- (2) Zollinger, H. *Colour Chemistry, Synthesis, Properties, and Applications of Organic Dyes*; Weinheim: New York, 1987.
- (3) Hartley, G. S. *Nature* **1937**, *140*, 281.
- (4) Nonnenberg, C.; Gaub, H.; Frank, I. *ChemPhysChem* **2006**, *7*, 1455–1461.
- (5) Bunce, N. J.; Ferguson, G.; Forber, C. L.; Stachnyk, G. J. *J. Org. Chem.* **1987**, *52*, 394–398.
- (6) Mostad, A.; Rømming, C. *Acta Chem. Scand.* **1971**, *25*, 3561–3568.
- (7) Coskun, A.; Banaszak, M.; Astumian, R. D.; Stoddart, J. F.; Grzybowski, B. *Chem. Soc. Rev.* **2011**, *41*, 19–30.
- (8) Blanco-Lomas, M.; Samanta, S.; Campos, P. J.; Woolley, G. A.; Sampedro, D. *J. Am. Chem. Soc.* **2012**, *134*, 6960–6963.
- (9) Bléger, D.; Liebig, T.; Thiermann, R.; Maskos, M.; Rabe, J. P.; Hecht, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 12559–12563.
- (10) Yager, K. G.; Barrett, C. J. *Macromolecules* **2006**, *39*, 9320–9326.
- (11) Wang, X.; Yin, J.; Wang, X. *Langmuir* **2011**, *27*, 12666–12676.
- (12) Yamada, M.; Kondo, M.; Mamiya, J.; Yu, Y.; Kinoshita, M.; Barrett, C. J.; Ikeda, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 4986–4988.
- (13) Yu, Y.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145–156.
- (14) Hampson, G. C.; Robertson, J. M. *J. Chem. Soc.* **1941**, 409–413.
- (15) Vapaavuori, J.; Priimagi, A.; Kaivola, M. *J. Mater. Chem.* **2010**, *20*, 5260–5264.
- (16) Jia, X.; Chao, D.; Berda, E. B.; Pei, S.; Liu, H.; Zheng, T.; Wang, C. *J. Mater. Chem.* **2011**, *21*, 18317–18324.
- (17) Goldenberg, L. M.; Kulikovskiy, L.; Gritsai, Y.; Kulikovskaya, O.; Tomczyk, J.; Stumpe, J. *J. Mater. Chem.* **2010**, *20*, 9161–9171.
- (18) Yager, K. G.; Barrett, C. J. *J. Chem. Phys.* **2007**, *126*, 94901–94908.
- (19) Yager, K. G.; Tanchak, O. M.; Godbout, C.; Fritzsche, H.; Barrett, C. J. *Macromolecules* **2006**, *39*, 9311–9319.
- (20) Barrett, C. J.; Natansohn, A. L.; Rochon, P. L. *J. Phys. Chem.* **1996**, *100*, 8836–8842.
- (21) Åstrand, P.-O.; Ramanujam, P. S.; Hvilsted, S.; Bak, K. L.; Sauer, S. P. A. *J. Am. Chem. Soc.* **2000**, *122*, 3482–3487.
- (22) Naito, T.; Horie, K.; Mita, I. *Macromolecules* **1991**, *24*, 2907–2911.
- (23) Paik, C. S.; Morawetz, H. *Macromolecules* **1972**, *5*, 171–177.
- (24) Naito, T.; Horie, K.; Mita, I. *Polymer* **1993**, *34*, 4140–4145.
- (25) Sekkat, Z.; Kleideiter, G.; Knoll, W. *J. Opt. Soc. Am. B* **2001**, *18*, 1854–1857.
- (26) Kleideiter, G. *J. Mol. Struct.* **2000**, *521*, 167–178.
- (27) *WiRE*, version 2.0 service pack 6; Renishaw plc: Wotton-under-Edge, Gloucestershire, U.K., 2002.
- (28) Mao, H. K.; Bell, P. M.; Shaner, J. W.; Steinberg, D. J. *J. Appl. Phys.* **1978**, *49*, 3276–3283.
- (29) Yager, K. G.; Barrett, C. J. *J. Chem. Phys.* **2004**, *120*, 1089–1096.
- (30) Nakatani, K.; Delaire, J. A.; Dumont, M.; Sekkat, Z.; Loucif-Saïbi, R. *Chem. Mater.* **1993**, *5*, 229–236.
- (31) Cook, A. H. *J. Chem. Soc.* **1938**, 876–881.
- (32) Fischer, E.; Frankel, M.; Wolovsky, R. *J. Chem. Phys.* **1955**, *23*, 1367–1368.
- (33) Janssen, J. F. *J. Chem. Educ.* **1969**, *46*, 117–118.
- (34) Holme, N. C.; Ramanujam, P. S.; Hvilsted, S. *Opt. Lett.* **1996**, *21*, 902–904.
- (35) Barrett, C. J.; Natansohn, A.; Rochon, P. *Chem. Mater.* **1995**, *7*, 899–903.
- (36) Ferraro, J. R. *Vibrational Spectroscopy at High External Pressures. Handbook of Vibrational Spectroscopy*; Academic Press, Inc.: New York, 2002.
- (37) Ferraro, J. R. *Vibrational Spectroscopy at High External Pressures: The Diamond Anvil Cell*; Academic Press, Inc.: New York, 1984.
- (38) Dias, A. R.; Minas da Piedade, M. E.; Martinho Simões, J. A.; Simoni, J. A.; Teixeira, C.; Diogo, H. P.; Meng-Yan, Y.; Pilcher, G. *J. Chem. Thermodyn.* **1992**, *24*, 439–447.
- (39) Dong, Z.; Seemann, N. M.; Lu, N.; Song, Y. *J. Phys. Chem. B* **2011**, *115*, 14912–14918.
- (40) Stuart, C. M.; Frontiera, R. R.; Mathies, R. A. *J. Phys. Chem. A* **2007**, *111*, 12072–12080.
- (41) Terao, F.; Morimoto, M.; Irie, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 901–904.
- (42) Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778–781.