

# Submolecular Plasticization Induced by Photons in Azobenzene Materials

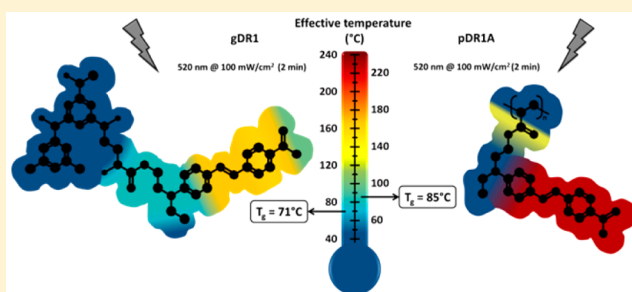
Jaana Vapaavuori,<sup>†,§</sup> Audrey Laventure,<sup>†,§</sup> C. Geraldine Bazuin,<sup>†</sup> Olivier Lebel,<sup>‡</sup> and Christian Pellerin<sup>\*,†</sup>

<sup>†</sup>Département de chimie, Centre de recherche sur les matériaux auto-assemblés (CRMAA/CSACS), Université de Montréal, Montréal, QC H3C 3J7, Canada

<sup>‡</sup>Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, ON Canada, K7K 7B4

**S** Supporting Information

**ABSTRACT:** We demonstrate experimentally for the first time that the illumination of azobenzene derivatives leads to changes in molecular environment similar to those observed on heating but that are highly heterogeneous at the submolecular scale. This localized photoplasticization, which can be associated with a free volume gradient, helps to understand the puzzling phenomenon of photoinduced macroscopic material flow and photoexpansion upon illumination far below the glass transition temperature ( $T_g$ ). The findings stem from the correlation of infrared (IR) spectral band shifts measured upon illumination with those measured at controlled temperatures for two amorphous DR1-functionalized azo derivatives, a polymer, pDR1A, and a molecular glass, gDR1. This new approach reveals that IR spectroscopy can be used as an efficient label-free molecular-scale thermometer that allows the assignment of an effective temperature ( $T_{\text{eff}}$ ) to each moiety in these compounds when irradiated. While no band shift is observed upon illumination for the vibrational modes assigned to backbone moieties of pDR1A and gDR1 and a small band shift is found for the spacer moiety, dramatic band shifts are recorded for the azo moiety, corresponding to an increase in  $T_{\text{eff}}$  of up to nearly 200 °C and a molecular environment that is equivalent to thermal heating well above the bulk  $T_g$  of the material. An irradiated azo-containing material thus combines characteristic properties of amorphous materials both below and above its bulk  $T_g$ . The direct measurement of  $T_{\text{eff}}$  is a powerful probe of the local environment at the submolecular scale, paving the way toward better rationalization of photoexpansion and the athermal malleability of azo-containing materials upon illumination below their  $T_g$ .



## INTRODUCTION

The repetitive photoisomerization of azobenzene derivatives, either covalently bonded or doped in glassy materials, can lead to photoinduced motion observable on macroscopic scales. This phenomenon has been exploited for the all-optical fabrication of nano- and microstructured surfaces,<sup>1,2</sup> for the tridimensional ordering of microphase-separated block copolymer structures,<sup>3</sup> as well as for the imaging of plasmonic structures.<sup>4</sup> However, a deeper understanding of the fundamentals governing this process is still required to fully take advantage of it. Indeed, how light can render glassy materials malleable at temperatures far below their bulk glass transition temperature ( $T_g$ ), often as much as 100 K, is currently one of the most puzzling questions in the materials science community. At such temperatures, the large-scale segmental motions of polymers are normally very slow or essentially frozen.<sup>5</sup>

Multiple approaches to address this paradox have been proposed, and there is an intensive debate about whether photoinduced motion is caused by a decrease of certain mechanical properties upon irradiation itself,<sup>6,7</sup> often referred to as photsoftening or photofluidization, or whether the

photoinduced orientation of the azo units can create stresses large enough to reshape materials in the glassy state.<sup>8</sup> The discussion is complicated by difficulties in the direct comparison of different methods used for measuring (bulk) mechanical properties and by ambiguity in what the terms “photsoftening” and “photofluidization” actually mean. They are sometimes understood metaphorically for describing softening that does not necessarily lead to a fluid-like state, and sometimes more literally to indicate the transformation of the material into a fluid-like state comparable to heating it above its bulk  $T_g$  into the viscoelastic flow region in the case of amorphous materials. The photoinduced melting of star-shaped azobenzene tetramers was recently demonstrated at ambient temperature, showing that isothermal light-powered fluidization of a crystal is possible.<sup>9</sup> For these reasons, building a unified and comprehensive picture of the state existing in azo-containing materials under illumination is rather challenging.

It is well established that the photoisomerization of azobenzenes requires greater volume than that occupied by

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either the (static) *trans* or *cis* isomers, thus generating additional free volume.<sup>10–13</sup> In particular, ellipsometry and neutron reflectometry studies have shown that irradiation leads to photoexpansion of the poly(Disperse Red 1 acrylate) (pDRIA) homopolymer at ambient temperature (around 60 °C below the bulk  $T_g$  for a molecular weight of ~5000 g/mol).<sup>14</sup> A pressure gradient resulting from different amounts of free volume created under an interference illumination pattern was also suggested as the driving force for all-optical surface patterning leading to the formation of surface relief gratings (SRGs),<sup>15</sup> although this view was criticized for not being able to account for the polarization dependence of SRG formation.<sup>1</sup> A similar photomechanical effect can be used to photoinduce bending of free-standing films due to the gradually diminishing light intensity in an absorbing material.<sup>16</sup>

There have been several attempts to directly observe photoinduced mechanical changes in azomaterials. Karageorgiev et al. conducted AFM-based indentation measurements and demonstrated a light-induced decrease in viscosity by many orders of magnitude as well as anisotropic polymer flow.<sup>17</sup> In support of this, Hurduc et al. observed the flow of actinic filaments on polysiloxane-based azopolymers under illumination of 488 nm light through fluorescence microscopy.<sup>18</sup> In this case, the photofluidization was strongly material dependent and was observed for cyano-tailed azobenzene side chains but not for  $\text{NO}_2$ - and H-tailed groups, which might be related to the higher capability of the former to promote a liquid crystalline mesophase. Fang et al. studied photofluidization from the viewpoint of relaxation dynamics and reported that, in dense self-assembled azo-containing monolayers under illumination by linearly polarized 514 nm light, only a few molecules are transiently heated to a temperature as high as 800 K, far above the  $T_g$  of most organic materials, whereas the overall material temperature increases by less than 1 K.<sup>19</sup> Finally, molecular simulations by Teboul et al. gave evidence of dynamic heterogeneities in glassy azo-containing materials.<sup>13,20</sup>

Herein, we probe the athermal malleability phenomenon from a molecular point of view, in contrast to a macroscopic point of view, by exploiting the selectivity of infrared spectroscopy (IR) with in situ temperature control and illumination of the materials. We thereby show experimental evidence for the first time that the repeated photoisomerization of azobenzenes induces changes in their molecular environment that are similar to those observed on bulk heating but that are heterogeneously distributed within individual molecules or molecular segments. We do this using two amorphous azomaterials, namely the pDRIA homopolymer and a DR1-containing mexylaminotriazine molecular glass,<sup>21</sup> gDR1 (a small organic molecule that readily forms an amorphous phase without requiring extreme processing conditions). Correlating the positions of IR bands associated with different molecular moieties under illumination of unpolarized 520 nm light with their positions at controlled temperatures leads to the concept of an effective temperature,  $T_{\text{eff}}$ , as an indicator of the local molecular environment under illumination. This novel label-free IR method allows observing a submolecular  $T_{\text{eff}}$  gradient under illumination that, in the case of pDRIA, is as large as 200 °C between the azo moiety and the backbone and that can be associated with a free volume gradient. Combined with the photo-orientation ability of azo moieties, this observation offers a plausible origin for photoinduced motion in azomaterials below their glass transition temperature.

## EXPERIMENTAL SECTION

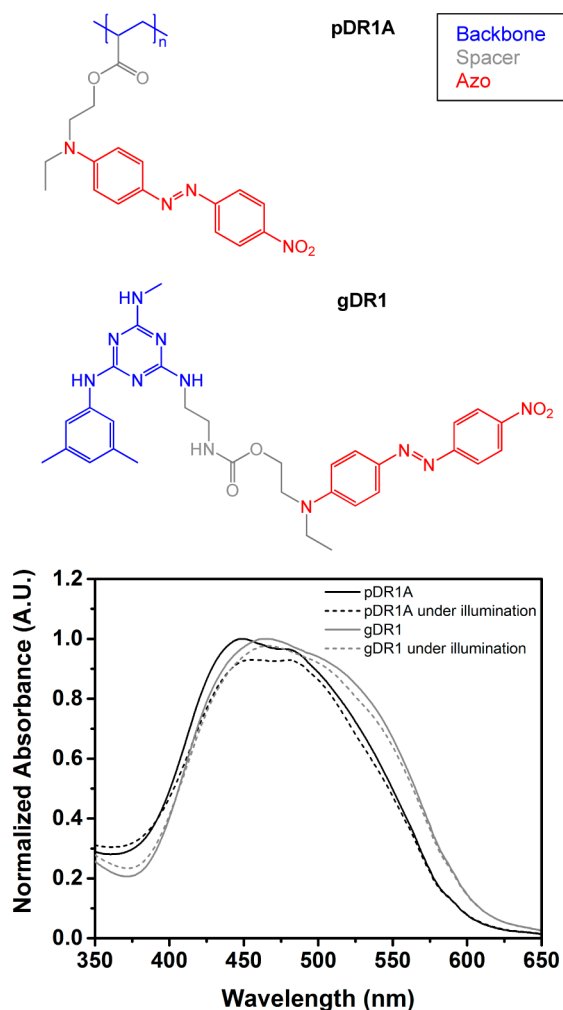
Solutions of pDRIA (Sigma-Aldrich, MW = 5000 g/mol) and gDR1 (synthesized according to literature procedures<sup>21</sup>) in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , respectively, were cast on the single reflection diamond element of a Heated Golden Gate (Specac) attenuated total reflection (ATR) accessory. Spectra were recorded using a Tensor 27 FT-IR spectrometer (Bruker Optics) equipped with a liquid nitrogen-cooled MCT detector. The samples were first heated to 140 °C followed by an isotherm of 3 min. Spectra were recorded during a cooling ramp at 2 °C/min by averaging 100 scans with a 4  $\text{cm}^{-1}$  resolution. Background scans were recorded for each sample temperature. After performing these heating and cooling cycles, which at the same time remove the thermal history of the materials, the samples were irradiated using a LED source (Prizmatix FC5Multichannel LED) at 520 nm with an irradiance of 10, 45, or 100  $\text{mW}/\text{cm}^2$ . Three repetitive cycles of 2 min darkness followed by 2 min irradiation were performed to confirm the repeatability of the photoinduced band shifts. An irradiance of 100  $\text{mW}/\text{cm}^2$  was used to compare the spectroscopic  $T_g$  of samples upon cooling in the presence or absence of illumination. Band positions were determined using the OPUS 6.0 software (Bruker Optics) from the center of gravity of the top 50% of the bands. This procedure provides band positions with an uncertainty better than 0.01  $\text{cm}^{-1}$  and thus enables following small band shifts with temperature or under illumination.<sup>22</sup> A nonphotoisomerizing control sample was prepared by dispersing 5 wt % of Nile Red (Sigma-Aldrich) in poly(methyl methacrylate) (PMMA, MW = 35 000 g/mol, Scientific Polymer Products). Films were cast from a  $\text{CHCl}_3$  solution and studied by IR spectroscopy as a function of illumination and temperature as described above.

UV–visible spectra were recorded on films spin-coated on microscope glass slides from the same sample stock solutions using an Ocean Optics 2000+ fiber-coupled spectrometer and a DH-mini light source. Films were annealed at 140 °C for 30 min and cooled slowly to ambient temperature to remove thermal history and ensure comparability with IR samples. Clean glass slides were used as a reference. Differential scanning calorimetry analyses were conducted with a PerkinElmer DSC 8500 calorimeter, calibrated with indium, using a heating rate of 10 °C/min. The  $T_g$ 's were determined, after an initial cycle of heating and cooling at 10 °C/min, as the average half-height of the heat capacity jump in the second and third heating scans.

## RESULTS AND DISCUSSION

The materials selected for this study, a polymer (pDRIA) and a molecular glass (gDR1) presented in Figure 1, are both derivatives of Disperse Red 1 (DR1), one of the most exploited azobenzene derivatives in photorelated studies because its push–pull character leads to rapid *trans*–*cis*–*trans* cycles upon illumination in the blue-green part of the visible spectrum. These materials form surface relief gratings (SRGs) efficiently under illumination of a light interference pattern at ambient temperature, well below their  $T_g$ .<sup>15,21,23</sup> To distinguish the behavior of the different chemical groups in these molecules, a color code is used throughout this article, where red refers to the azo moiety, gray to the spacer, and blue to the backbone parts of the molecules.

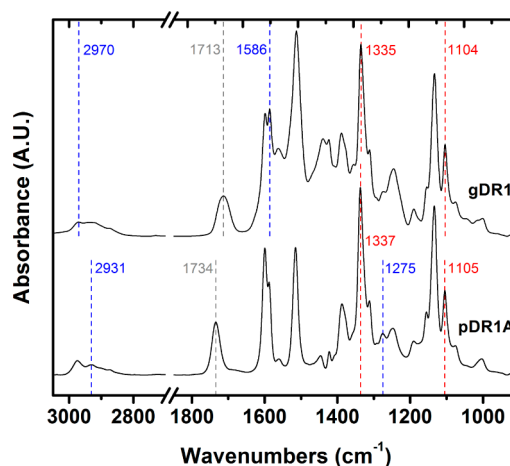
Figure 1 also shows that the UV–visible absorbance spectra of thin films of pDRIA and gDR1 are comparable both in terms of close absorption maxima (445 and 463 nm, respectively) and in terms of the asymmetric shape of the absorption band related to enhanced dipole–dipole interactions between adjacent DR1 units in the solid state.<sup>24</sup> Irradiation with unpolarized light at 520 nm results in photostationary states consisting primarily of *trans* isomers, with less than 5% and 10% of *cis* isomers for gDR1 and pDRIA, respectively, due to the fact that the illumination wavelength falls within the relatively broad range absorbed by both *trans* and *cis* isomers of DR1



**Figure 1.** Molecular structure and UV–visible absorbance spectra of pDR1A and gDR1 before (plain lines) and under (dotted lines) irradiation. A color scheme highlights the azobenzene (red), spacer (gray), and backbone (blue) moieties of the molecules.

(thus driving both *trans*–*cis* and *cis*–*trans* photoisomerization reactions)<sup>25</sup> and that the thermal relaxation lifetime of DR1-type chromophores is on the order of seconds.<sup>26</sup> In addition to enabling efficient photoinduced mass transport, this photostationary state with a low *cis*-isomer concentration facilitates correlating the IR spectroscopy results upon illumination and at controlled temperature because complications due to the presence of bands of the *cis* isomers in the spectra under illumination are mainly avoided.

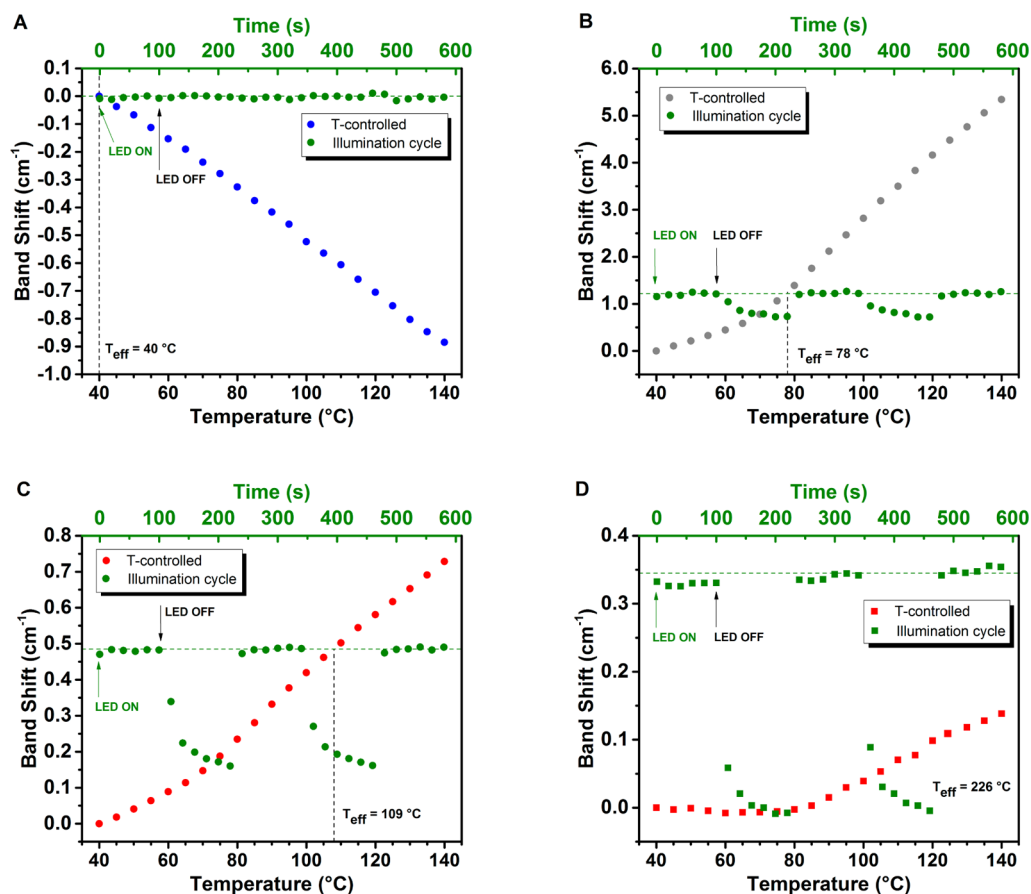
We use IR spectroscopy as a powerful label-free probe to investigate how photoisomerization influences the azo materials on a molecular level because the position, shape and width of IR bands all depend on the molecular environment of the absorbing chemical groups of the compound under study.<sup>22,27</sup> The IR spectra of the compounds investigated here are presented in Figure 2. The assignments of the bands of importance for this study are collected in Table S1 (Supporting Information).<sup>28</sup> To determine how photoisomerization affects different parts of the molecules, bands that are associated primarily with the azo (red), spacer (gray), and backbone (blue) moieties are color-coded as shown in Figure 1. Great care was taken to avoid overlapped bands due to vibrational modes involving multiple parts of the molecules.



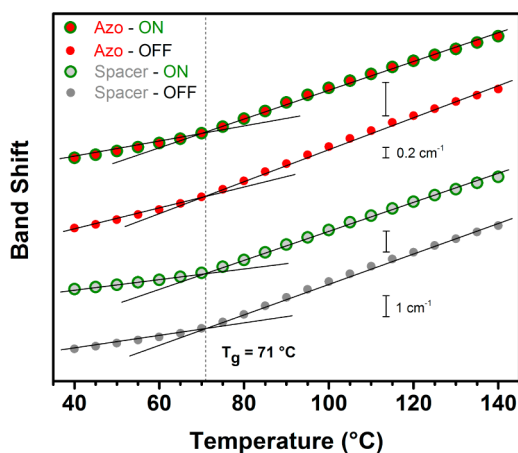
**Figure 2.** IR spectra of pDR1A and gDR1 showing selected vibrational modes associated with the azo (red), spacer (gray), and backbone (blue) moieties of the molecules.

Figure 3 shows the observed band shifts (with reference to the position of the band at 40 °C without illumination) for representative functional groups from the backbone, spacer and azo moieties of gDR1 and for the azo group of pDR1A (results for the spacer and backbone of pDR1A are given in Figure S1 of the SI) as the sample is cooled from 140 °C, which is well above the  $T_g$  (data colored according to the code of Figure 1, bottom X axis), and when cyclic illumination is applied at a constant temperature of 40 °C (data in green, top X axis). A gradual band shift is clearly observed when the temperature of the sample is changed. The evolution of band position as a function of temperature often allows determining phase transition temperatures because it reflects the perturbation of the molecular environment. First-order phase transitions, such as a melting event, can be observed spectroscopically as an abrupt change in band position at the transition temperature,<sup>29</sup> similar to the jumps observed when measuring the specific volume or the enthalpy.<sup>5</sup> Since the glass transition of amorphous materials is a pseudo-second order transition, a change of slope is expected at the transition temperature.<sup>5,30,31</sup> Indeed, a change of slope upon cooling gDR1 is clearly observable in Figure 3B and C at 71 °C, a temperature that corresponds to its bulk  $T_g$ <sup>32</sup> as determined by differential scanning calorimetry (DSC). A similar change of slope upon cooling is observed at 85 °C for pDR1A in Figure 3D, which similarly corresponds to its bulk  $T_g$  value determined by DSC. The positions of the selected IR bands are thus indicators of the molecular environment of the moieties involved. It should be noted here that, as will be shown in Figures 4 and S2, the spectroscopic  $T_g$  of gDR1 and pDR1A are not affected under the illumination conditions applied.

When the samples are irradiated with 520 nm light, a clear shift is observed for the bands associated with the azo and spacer moieties even though the bulk temperature of the sample remains fixed at 40 °C. The repeatability of the photoinduced band shifts, clearly observable in Figure 3B–D during consecutive cycles of 120 s of illumination (LED on) followed by 120 s of relaxation in darkness (LED off) (data in green, top X axis), indicates that the transient modification of the molecular environment upon photoisomerization is repeatable, as previously shown in photoexpansion studies of pDR1A by Barrett and co-workers using ellipsometry measurements.<sup>14</sup> When the thermally induced and photoinduced band



**Figure 3.** Procedure for determining the effective temperature ( $T_{\text{eff}}$ ) of the chemical groups by comparison of the IR band shifts under illumination cycles at 40 °C (green) and in the dark during temperature ( $T$ )-controlled ramps (see text for details). Examples are shown for the gDRI (A) backbone (1586 cm<sup>-1</sup> triazine ring stretching), (B) spacer (1713 cm<sup>-1</sup> C=O stretching), and (C) azo (1335 cm<sup>-1</sup> NO<sub>2</sub> symmetric stretching) bands and for the pDR1A (D) azo (1337 cm<sup>-1</sup> NO<sub>2</sub> symmetric stretching) band.



**Figure 4.** Evolution of the band shifts (gray, spacer C=O stretching; red, azo NO<sub>2</sub> symmetric stretching) of gDRI on cooling without (“OFF”) and with (“ON”) illumination at 520 nm using an irradiance of 100 mW/cm<sup>2</sup>. The change in slope corresponds to the  $T_g$  of the material as determined by DSC.

shifts are compared, the most striking observations are that they systematically evolve in the same direction and that the amplitude of the photoinduced band shifts increases with increasing proximity of the chemical group to the azo moiety. More specifically, as compared to the effect of raising the bulk sample temperature, no significant band shift is observed under

illumination for the backbone (Figure 3A), a relatively small shift is observed for the spacer (Figure 3B) and a much larger relative shift occurs for the azo (Figure 3C). Similar observations for pDR1A are shown in Figures 3D and S1. In this case, the photoinduced band shift for the azo moiety (Figure 3D) is even more than twice the band shift recorded upon heating from 40 to 140 °C.

These observations legitimately raise the question of whether illumination decreases the bulk  $T_g$  of the materials. To verify this,  $T_g$ 's were determined spectroscopically using IR band shifts measured under the conditions of interest. Figure 4 displays the band shift of gDRI as a function of temperature during cooling ramps under irradiation (data with green edges) and without irradiation (data without green edges) for the carbonyl stretching (1713 cm<sup>-1</sup>, in gray) and NO<sub>2</sub> symmetric stretching (1335 cm<sup>-1</sup>, in red) bands. Both experimental conditions lead to an identical  $T_g$  of 71 °C for gDRI and of 85 °C for pDR1A (see Figure S2 in SI), in exact agreement with the values obtained for bulk samples by DSC using a 10 °C/min heating ramp. These results unambiguously show that the overall spectroscopic  $T_g$  of the materials is unaffected by photoisomerization upon illumination under the conditions used, and are in accordance with the results of Fang et al. showing no significant illumination-related temperature increase in their material despite their observation of an uneven distribution of heated molecular environments.<sup>19</sup> This conclusion is reinforced by the fact that the backbone moieties for

both samples show no measurable photoinduced band shift, indicating that their molecular environment is identical with and without illumination, thereby preventing isotropic flow of the bulk sample upon illumination.

The specific position of an IR absorption band depends on the force constant and the reduced mass of its associated vibrating dipole. The band shifts observed as a function of temperature and under illumination are therefore due to the concomitant evolution of several aspects affecting the local molecular environment of the absorbing groups, including the strength of intermolecular interactions, the local conformation, and the level of stress acting on the bonds.<sup>22,27</sup> The fact that the band shifts observed in Figures 3 and S1 (as well as for the other bands studied but not shown) systematically occur in the same direction when increasing the temperature and when illuminating the sample, strongly suggests that they share the same molecular origin. The most plausible common origin is the generation of additional free volume in the sample, which would provoke the observed band shifts by decreasing the strength of local intermolecular interactions (by increasing the average molecular distance) and by enabling more freedom to explore the molecular conformational space. Indeed, it is known from photoexpansion studies that repeated *trans*–*cis*–*trans* cycling introduces free volume under illumination,<sup>10,14,33</sup> and that heating amorphous materials also increases their free volume (note that the band shifts observed in Figures 3 and 4 are very similar to the temperature dependence of specific volume).<sup>5,31</sup>

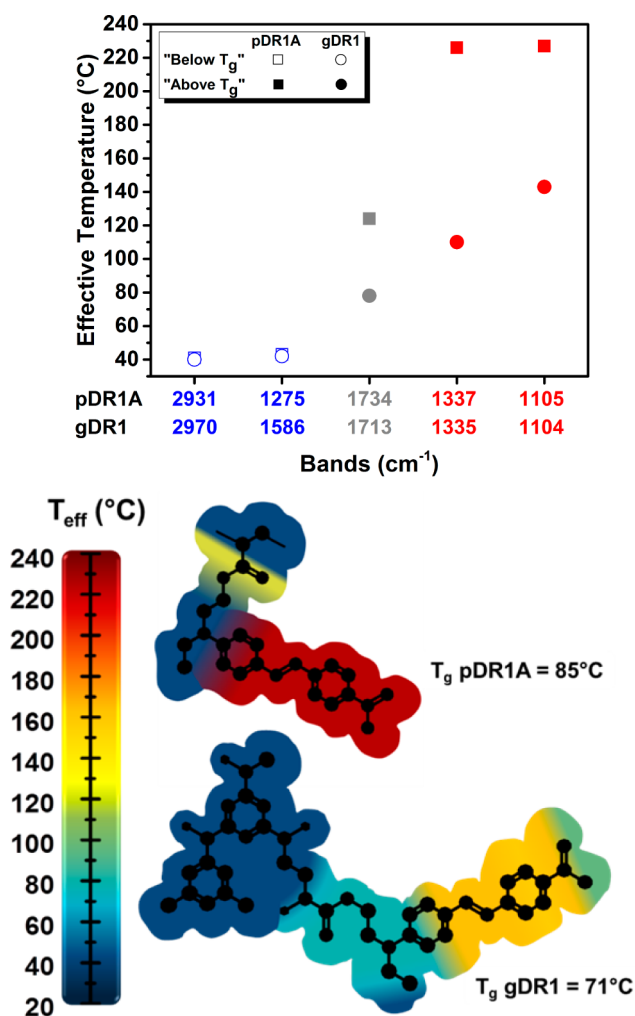
A possible alternative interpretation is that the apparent local heating is due to heat dissipation from nonradiative transitions in the chromophore. To rule this out, a sample analogous to pDR1A structurally and spectrally but that does not photoisomerize was prepared by dispersing Nile Red in PMMA. This blend absorbs strongly at the excitation wavelength of 520 nm (its absorption maximum is at 528 nm; see Figure S3A) and presents IR bands that are well isolated for Nile Red and relatively well isolated for PMMA (Figure S3B). Figure S4 shows clear shifts of these bands, along with a change in slope at the PMMA  $T_g$  for some bands, upon physically heating the sample, which is very similar to the behavior in gDR1 and pDR1A. In contrast, there is no significant shift for any of these bands under irradiation (Figure S4). Even though the number density of absorbing molecules in this Nile Red/PMMA blend is lower than in gDR1 or pDR1A, the lack of photoinduced shift for the Nile Red bands indicates that local heating due to dissipation of the photon energy does not contribute significantly to the observed band shifts for DR1-containing systems. This result is in agreement with the recently observed athermal photoinduced melting of azobenzene crystals.<sup>9</sup> Furthermore, it confirms the importance of photoisomerization in the observed spectral changes described above and supports the interpretation that free volume plays an important role in the behavior of gDR1 and pDR1A under illumination.

In this context, the similarity of the band shifts observed under illumination and upon heating observed in Figure 3 reveal for the first time that illuminating a material capable of photoisomerization induces changes in the molecular environment that are heterogeneously distributed along a single molecule (gDR1) or polymer repeat unit (pDR1A). Since the azo moiety is the group that directly interacts with light, undergoing repeated *trans*–*cis*–*trans* isomerization, the local increase in free volume under illumination is greatest around the azo groups and diminishes with molecular distance from

this group, while the glass and the polymer backbone environments are essentially unaffected. In contrast, the increase in free volume introduced by heating the sample is more or less uniformly distributed at the molecular level, leading to band shifts for all of the moieties, azo, spacer and backbone.

These results indicate that certain parts of the molecules experience a local environment under illumination that is analogous to that found at temperatures above, even far above, the  $T_g$  of the material while the bulk temperature remains unaffected. This gives rise to the concept that IR can be used as a submolecular “thermometer”. Indeed, correlating the photoinduced band shift with the bulk temperature that gives the same band shift allows the determination of a photoinduced “effective temperature”,  $T_{\text{eff}}$  independently for each molecular moiety that is being probed. In other words, we use  $T_{\text{eff}}$  as an indicator to describe the temperature to which the material must be heated to reproduce the band position (and thus the molecular environment) that is observed under irradiation. It must be stressed, however, that  $T_{\text{eff}}$  should not be taken literally as the physical temperature of a chemical group. It should also be noted that the amplitude of the band shift with (bulk) temperature is different for each band, and thus the effect of irradiation must be considered in relative terms with respect to the effect of temperature. As an example, Figure 3B shows that the C=O band of gDR1 is at the same position under illumination (indicated by the green dashed line) and when heated to 78 °C (highlighted by the black dashed line). Its effective temperature under illumination is therefore 78 °C. (It is of interest to mention that illumination for 120 s is long enough to reach a plateau in the band position for gDR1 but that a slight increase in band shift is observed between cycles for pDR1A, suggesting that reaching a plateau  $T_{\text{eff}}$  requires a longer illumination time for this polymer.) After the light is switched off, the band positions, and thus  $T_{\text{eff}}$ , gradually return toward the bulk temperature of 40 °C. For some functional groups (Figure 3B and C), a much longer recovery time than 120 s is needed to return to the initial state, which must be related to the movement of glassy matrices that are known to be relatively slow at temperatures below  $T_g$  and is a topic for a future study.

The effective temperatures achieved under illumination with an irradiance of 100 mW/cm<sup>2</sup> were determined for all of the bands investigated as illustrated in Figure 3 and were highly reproducible from sample to sample. They are reported in Figure 5 in graphical form (top), where the filled and open symbols represent  $T_{\text{eff}}$ 's that are above and below the bulk  $T_g$  of the material, respectively, and in a color-coded molecular representation (bottom). When the band shifts upon illumination exceed those observed as a function of temperature, such as for the NO<sub>2</sub> vibration of pDR1A (see Figure 3D), the curve of the band shift as a function of temperature is extrapolated linearly. The behavior of the azo moiety (in red) under illumination is particularly striking. For the symmetric NO<sub>2</sub> vibration at about 1336 cm<sup>-1</sup>, the effective temperature under illumination reaches 226 °C (160% higher than the temperature at which the illumination experiment was conducted, i.e. 40 °C) for pDR1A and 109 °C (120% higher than the bulk temperature) for gDR1. These enormous increases in  $T_{\text{eff}}$  for the azobenzene moiety are confirmed by the corresponding values of 227 and 143 °C, respectively, obtained for the azobenzene aromatic ring deformation band at about 1105 cm<sup>-1</sup>. Thus, the vibrational modes located near the



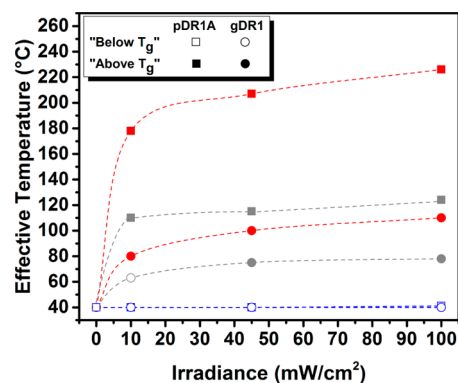
**Figure 5.** Top: Effective temperatures ( $T_{\text{eff}}$ ) of pDR1A (squares) and gDR1 (circles) bands at 40 °C under irradiation at 520 nm (100 mW/cm<sup>2</sup>). Blue refers to the backbone bands, gray the spacer bands, and red the azo bands. Open and filled symbols indicate a  $T_{\text{eff}}$  below and above the bulk  $T_g$ , respectively. Bottom: Molecular representation of  $T_{\text{eff}}$  according to the color-coded scale.

azo chemical function, which, according to current understanding,<sup>34</sup> undergoes either rotation, inversion, concerted inversion or inversion-assisted rotation upon photoisomerization, feel a molecular environment that, in terms of effective temperature, is equivalent to heating well above the bulk  $T_g$  of the materials.

In sharp contrast to the azobenzene bands, the effective temperature upon illumination of the backbone bands remains identical to the bulk temperature, within experimental uncertainty, and is thus more than 30 °C below the bulk  $T_g$  in both materials. The C=O groups in the spacers, in gray, present an intermediate behavior, with  $T_{\text{eff}}$ 's of 124 and 78 °C for pDR1A and gDR1, respectively, which are higher than the experimental isothermal 40 °C, but much less than for the azo groups. They are also higher than the bulk  $T_g$  but by only 7 °C for gDR1. These values of  $T_{\text{eff}}$  indicate that the local environment of the C=O groups is influenced even if they are relatively far from the photoisomerizing azo groups.

Since photoinduced mass transport during SRG patterning is reported to depend on the incident irradiance,<sup>15,21</sup> the impact of illumination intensity on the effective temperature of the

different molecular groups was also studied. As shown by Figure 6, the effective temperatures are intensity-dependent



**Figure 6.** Influence of the 520 nm irradiance on the effective temperature of bands associated with the backbone (blue), spacer (gray), and azo (red) moieties of pDR1A and gDR1 (the NO<sub>2</sub> symmetric stretching was chosen as the representative band for the azo moiety). Dashed lines are guides to the eye.

except for the backbones that do not show any discernible increase in  $T_{\text{eff}}$  even at the highest intensity investigated (100 mW/cm<sup>2</sup>). For the azobenzene and spacer groups, the increase in  $T_{\text{eff}}$  as a function of intensity is not linear but seems to tend toward saturation. This observation is in line with the nonlinear increase in SRG diffraction efficiency as a function of irradiance.<sup>21</sup> It is also consistent with molecular dynamics simulations predicting saturation of the diffusion coefficient of a glass-forming host when a guest azobenzene undergoes high frequency photoisomerization at high intensities.<sup>12</sup> Moreover, the overall effective temperatures are systematically lower, at all irradiances, for gDR1 than for pDR1A. This difference could originate from the hydrogen-bonded network formed by these molecules.<sup>35</sup> As shown in Figure S5, these noncovalent interactions remain intact upon illumination, providing still more evidence that cooperative motions of repeat units (for polymers) or complete molecules (for molecular glasses) are not directly affected by photoisomerization. The hydrogen bonds in gDR1 appear to restrict the mobility of the chemical groups, and thus the extent of the photoinduced changes in molecular environment, to a greater extent than the van der Waals interactions among pDR1A side chains.

The inhomogeneous distribution of effective temperature under irradiation can be mapped on the structures of gDR1 and pDR1A according to a color-coded scale, as shown in Figure 5 (bottom). It illustrates the creation of submolecular areas with higher mobility (higher  $T_{\text{eff}}$ ), as previously hypothesized to explain the photoinduced diffusion and modification of mechanical properties in azomaterials.<sup>12,13,19,20</sup> Thus, amorphous azo-containing materials under illumination present the properties of both glassy (backbone) and fluid-like (spacer and azo moieties) materials below their bulk  $T_g$ . This combination of characteristics generated in the “photomobile” state of azo-containing materials is in agreement with simulations by Accary and Teboul that suggested the appearance of soft regions around photoisomerizing azobenzenes dispersed in a more viscous glassy material.<sup>12</sup>

It is noteworthy that these results were obtained for bulk three-dimensional thin films and thus complement the results of Fang et al.<sup>19</sup> and Hurduduc et al.,<sup>18</sup> who studied similar phenomena (although not at the submolecular scale) in self-

assembled monolayers and at the surface of the material, respectively, where the diffusion rate is already orders of magnitude faster than in the bulk, making it more difficult to clearly dissociate photoinduced fluidity from the intrinsic fluidity of the materials.<sup>36</sup>

The significance of this experimental demonstration of a heterogeneous generation of photoinduced free volume around specific molecular moieties, as revealed by their larger relative increase in  $T_{\text{eff}}$  under illumination, resides in the fact that it helps to account for a wide array of puzzling photoinduced phenomena involving azo-containing materials at scales ranging from molecular to macroscopic. Our experimental results relate to some early conclusions made in the 1990s by Kumar et al. on the plasticizing effect of light on azopolymers during SRG writing<sup>37</sup> and also to the creation of free volume upon isomerization of azobenzenes reported by Bauer-Gogonea et al.<sup>33</sup> It also supports the very recently reported vaporization of liquid water by Fujiwara and Imura upon photoisomerization of azobenzene-modified anodized alumina filtration membranes:<sup>38</sup> these authors proposed that low density areas, created upon photoisomerization, correspond to low-pressure zones that facilitate the evaporation and transport of water molecules across the membrane. These low-pressure zones could also support the hypothesized worm-like (directional along the main molecular axis) diffusion motion, first proposed by Lefin and Nunzi,<sup>39</sup> and further developed by Juan et al. to account for polymer motion both during SRG formation<sup>40</sup> and under nanoplasmonic fields.<sup>7</sup> Based on the results, one can further anticipate that, as long as the photochemistry of the azobenzene group is preserved, increasing the bulkiness of the azobenzene substituent should increase the effective temperature gradient along the molecule and favor phototransport by creating a larger fraction of free volume under irradiation. This hypothesis is consistent with the experimental evidence showing that greater bulkiness of azo groups increases their SRG forming capacity.<sup>41</sup> Moreover, a local increase of free volume near the azo moiety could account more realistically for the modification of the material's mechanical properties, by opposition to a truly fluid-like state reached upon illumination.<sup>17</sup> Indeed, a true liquid-like state must not be reached at any point during photoprocessing; if so, it would lead to the erasure of the light-written pattern due to fast relaxation of the material. In contrast, a submolecular free volume gradient, as suggested in the present work, can account both for light-induced motion and for its temporal stability.

## CONCLUSION

We have shown by IR spectroscopy that the sub- $T_g$  illumination of amorphous azomaterials, both polymers (pDRIA) and molecular glasses (gDR1), provokes changes in local environment that are highly heterogeneous at the submolecular scale. To quantify these relative changes, the concept of an effective temperature ( $T_{\text{eff}}$ ) was introduced, corresponding to the bulk temperature to which the chemical group in question must be heated in order to reproduce the IR band shift measured under illumination. The change in local environment of the azo moiety upon photoisomerization corresponds to an increase in  $T_{\text{eff}}$  of up to nearly 200 °C, while, in sharp contrast, the local environment of the backbone does not change at all. On the basis of the similarity of the band shifts upon heating and under illumination, two processes known to introduce additional free volume in amorphous (azo)materials, the results are interpreted as evidence for a submolecular gradient of photoinduced free

volume. Meanwhile, the bulk  $T_g$  of the materials remains unaffected by illumination, at least up to an intensity of 100 mW/cm<sup>2</sup>, highlighting that the mechanism leading to the photomobile state, which allows macroscopic motion in azomaterials, is inherently different from the fluidization of the material occurring upon heating above its  $T_g$ . The experimental observation of a heterogeneous distribution of  $T_{\text{eff}}$  in individual molecules complements the existing evidence for mechanical property modifications under irradiation and offers a general molecular-level picture for how light enables these photoresponsive materials to move remarkable distances at temperatures well below their  $T_g$ . The IR method presented here could also be used as a submolecular probe of molecular environment perturbations under the application of various other external stimuli, such as electric or magnetic fields, thus broadening the interest of this label-free approach.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06611.

Attribution of the IR bands and additional results for pDRIA and gDR1. UV–visible and IR spectroscopy results for the Nile Red/PMMA blend (PDF)

## AUTHOR INFORMATION

### Corresponding Author

\*c.pellerin@umontreal.ca

### Author Contributions

§J.V. and A.L. contributed equally.

### Notes

The authors declare no competing financial interest.

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