

# Regioisomer-Specific Mechanochromism of Naphthopyran in Polymeric Materials

Maxwell J. Robb,<sup>†,‡</sup> Tae Ann Kim,<sup>†,§</sup> Abigail J. Halmes,<sup>†,‡</sup> Scott R. White,<sup>†,||</sup> Nancy R. Sottos,<sup>\*,†,§</sup> and Jeffrey S. Moore<sup>\*,†,‡</sup>

<sup>†</sup>The Beckman Institute for Advanced Science and Technology, <sup>‡</sup>Department of Chemistry, <sup>§</sup>Department of Materials Science and Engineering, and <sup>||</sup>Department of Aerospace Engineering, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States

**S** Supporting Information

**ABSTRACT:** Transformation of naphthopyran into a colored merocyanine species in polymeric materials is achieved using mechanical force. We demonstrate that the mechanochemical reactivity of naphthopyran is critically dependent on the regiochemistry, with only one particular substitution pattern leading to successful mechanochemical activation. Two alternative regioisomers with different polymer attachment points are demonstrated to be mechanochemically inactive. This trend in reactivity is accurately predicted by DFT calculations, reinforcing predictive capabilities in mechanochemical systems. We rationalize the reactivity differences between naphthopyran regioisomers in terms of the alignment of the target C–O pyran bond with the direction of the applied mechanical force and its effect on mechanochemical transduction along the reaction coordinate.

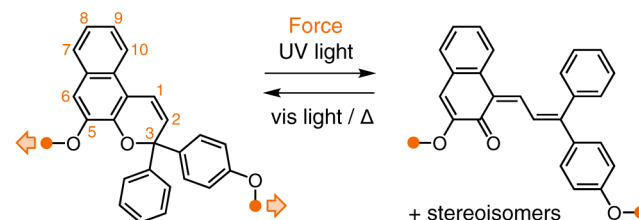
Polymer mechanochemistry is an emerging field of research in which mechanical forces are harnessed to promote selective chemical transformations.<sup>1</sup> Polymers serve the critical role of transducing a mechanical load to a particular covalent bond within a mechanochemically active molecule, called a mechanophore.<sup>2</sup> Mechanochromic molecular force probes provide a convenient route for visually identifying critical stress and/or strain in a material as well as recording its mechanical history. In addition to the extensively studied spiropyran–merocyanine system,<sup>3</sup> several other mechanochromic mechanophores have been developed, including diarylbenzofuranone<sup>4</sup> and hexaarylbiimidazole,<sup>5</sup> which fragment under mechanical stress to generate colored free radicals. The mechanochromic behavior of a rhodamine-based mechanophore<sup>6</sup> and spirothiopyran<sup>7</sup> has also recently been demonstrated. In contrast to the large deformations typically required to achieve mechanophore activation in the bulk,<sup>3,8</sup> the development of mechanophores for epoxy-based thermoset polymers<sup>9</sup> has led to mechanochromic composite materials that activate at relatively low strain thresholds.

Despite the growing repertoire of covalent mechanophores,<sup>10</sup> a more complete understanding of structure–mechanochemical activity relationships will drive further innovation.<sup>11</sup> Molecular geometry, in particular, has a significant influence on mechanochemical reactivity. For example, cyclobutane-based mechanophores are sensitive to stereochemistry, with cis

diastereomers being more reactive than trans diastereomers.<sup>12</sup> Similarly, stereoisomers of *gem*-dihalocyclopropane<sup>13</sup> and benzocyclobutene<sup>13a,14</sup> mechanophores react with different threshold forces that favor activation of the cis diastereomers. A few reports have also highlighted the importance of regiochemistry. Varying the polymer attachment points on spiropyran results in different threshold forces for activation.<sup>15</sup> Computational studies also indicate that a mechanically facilitated [4 + 2] cycloreversion of the 1,2,3-triazole moiety is predicted for the 1,5-regioisomer, whereas the 1,4-regioisomer undergoes homolytic cleavage of bonds adjacent to the triazole ring for experimentally relevant models.<sup>16</sup> Mechanical force has been demonstrated to suppress the reactivity of an anthracene–maleimide adduct with a particular substitution pattern by increasing the reaction energy barrier,<sup>17</sup> while a similar phenomenon has also been observed for the cyclobutane-1,3-dione moiety.<sup>18</sup> Beyond the structure of the mechanophore itself, the geometry of the attached polymers also affects the reactivity.<sup>19</sup> A so-called backbone lever-arm effect, for instance, significantly enhances mechanical activity by providing a greater mechanical advantage.<sup>20</sup>

Here we introduce a new mechanochromic mechanophore based on naphthopyran, specifically the 3*H*-naphtho[2,1-*b*]pyran skeleton (Scheme 1). Similar to spiropyran, naphthopyrans are well-known photochromic molecules that reversibly transform into colored merocyanine species under UV light via a 6 $\pi$  electrocyclic ring-opening reaction.<sup>21</sup> We investigate the mechanochemical activation of three different

**Scheme 1. Transformation of Naphthopyran into a Colored Merocyanine Species Is Accomplished Using Mechanical Force<sup>a</sup>**



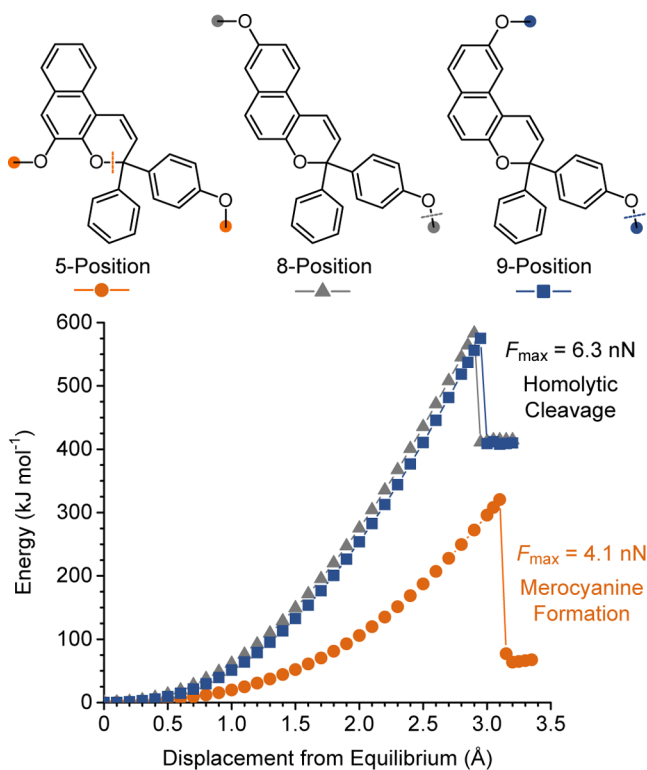
<sup>a</sup>The numbering system of 3*H*-naphtho[2,1-*b*]pyrans is illustrated.

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naphthopyran regioisomers in bulk polymeric materials and find that only one regioisomer exhibits mechanochromic properties, validating predictions from density functional theory (DFT) calculations. A geometrical analysis provides insight into the regioisomer-specific reactivity of naphthopyran and reinforces mechanophore design.

DFT calculations using the simple computational technique, constrained geometries simulate external force (CoGEF),<sup>22</sup> were initially performed to investigate the mechanochemical reactivity of naphthopyrans (Figure 1). Three different



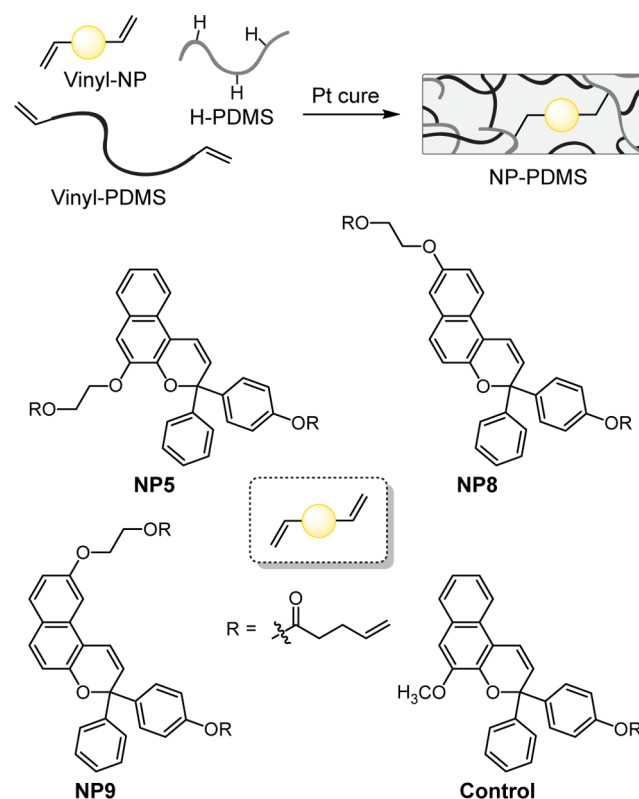
**Figure 1.** DFT calculations (CoGEF) for three naphthopyran regioisomers predict regioisomer-specific mechanochemical reactivity. Cleavage of the C–O pyran bond and transformation to the merocyanine species is predicted only for the naphthopyran regioisomer substituted at the 5-position. Calculations were performed at the B3LYP/6-31G\* level of theory.

regioisomers were studied, varying the position of the methoxy group on the naphthalene ring. Starting from the equilibrium geometry of each molecule, the distance between the methyl groups was increased, and the constrained geometry was optimized at distinct intervals of elongation. Interestingly, the naphthopyran substituted at the 5-position exhibited selective cleavage of the C–O pyran bond and successful transformation to the merocyanine species with an estimated rupture force of 4.1 nN. In direct contrast, however, the naphthopyran regioisomers substituted at the 8- and 9-position were both predicted to undergo homolytic cleavage of one of the methyl ether bonds at a significantly greater force of 6.3 nN.

Intrigued by the computational results, we set out to examine the mechanical activation of the naphthopyran series in bulk polymeric materials. Naphthopyrans were readily synthesized via the acid-catalyzed reaction between appropriately substituted 2-naphthols and 1-(4-hydroxyphenyl)-1-phenylprop-2-yn-1-ol (see the Supporting Information (SI) for details). Initial monosubstitution of the dihydroxynaphthalene substrates with

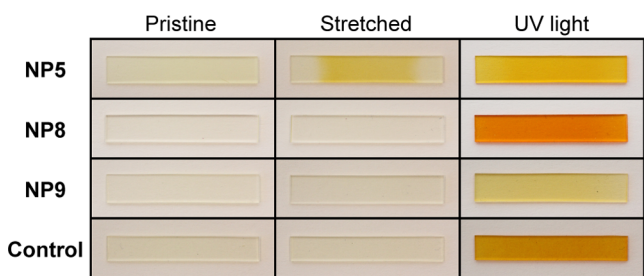
a hydroxyethyl group improved the efficiency of the naphthopyran synthesis while maintaining a reactive handle for subsequent functionalization. In a second step, naphthopyrans were functionalized with 4-pentenoic anhydride to facilitate their covalent incorporation into polydimethylsiloxane (PDMS),<sup>23</sup> which is an easily accessible polymeric testing platform (Scheme 2). Control experiments confirmed that the

### Scheme 2. Preparation of PDMS Materials with Covalent Incorporation of Three Different Naphthopyran Regioisomers and a Monofunctional Control



double bond of the pyran ring is unreactive toward Pt-catalyzed hydrosilylation, as expected (see the SI for details). In addition to the three bis(alkene)-functionalized naphthopyran regioisomers (NP5, NP8, and NP9), a naphthopyran control molecule containing a single vinyl group for covalent attachment within a PDMS network was prepared. Since mechanical force is not transferred across the molecule, the control distinguishes between reactivity that is mechanical in nature or originating from an alternative (e.g., thermal) mechanism.

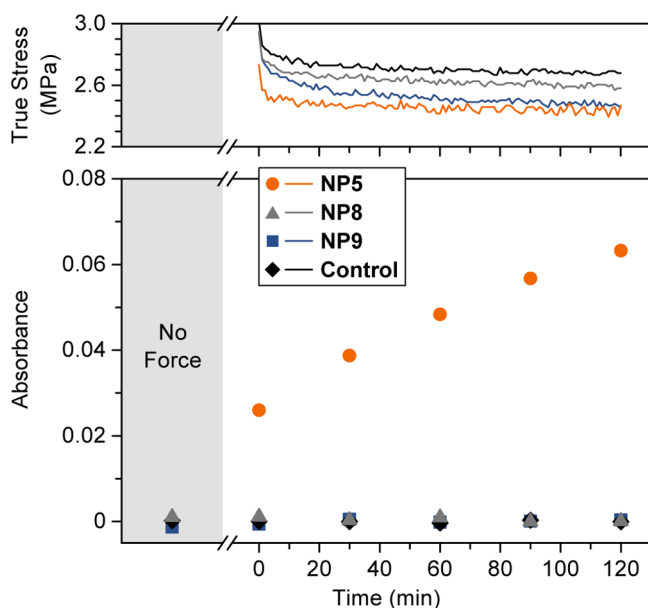
We began by investigating PDMS films covalently incorporating the three bis(alkene)-functionalized naphthopyran regioisomers and the monofunctional control (Figure 2). The materials, which were prepared with an approximately 1.5 wt % loading of each naphthopyran, are clear and very slightly yellow in color. Consistent with the CoGEF calculations, stretching PDMS films incorporating NP5 connected at the 5-position causes the gauge region of the material to turn orange-yellow in color, suggesting mechanochemical transformation of the naphthopyran into the merocyanine species (see the movie in the SI). Under ambient conditions, the color fades relatively quickly (on the order of several minutes) as the merocyanine form is converted back into the naphthopyran. Importantly, no



**Figure 2.** Photographs of PDMS materials incorporating naphthopyrans after application of mechanical force (tension) and UV light. Only the PDMS material containing naphthopyran substituted at the 5-position (NP5) changes color upon stretching. Scale bar = 1 cm.

color change is observed upon mechanical stretching of the PDMS materials incorporating either of the other regioisomers NP8 and NP9 or the naphthopyran control. Illumination with 365 nm UV light, however, causes all of the PDMS materials to change color, confirming the presence of the naphthopyran molecules.

Mechanical testing combined with in situ visible absorption measurements enabled further characterization of the mechanochemical properties of the materials (Figure 3). PDMS

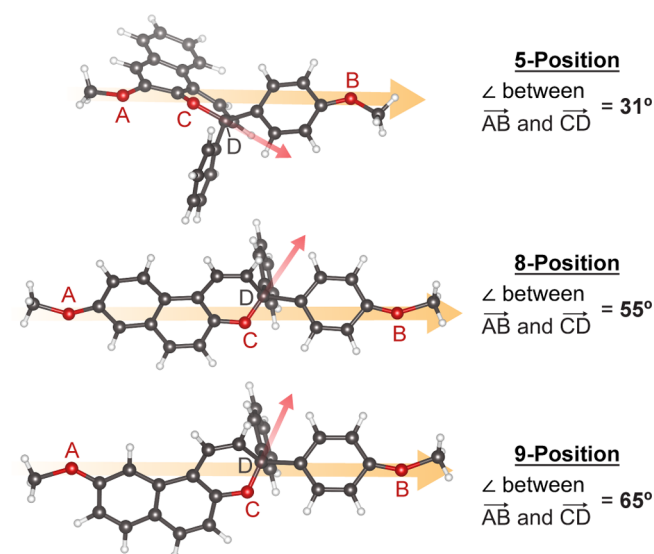


**Figure 3.** Visible absorption of PDMS materials incorporating naphthopyran regioisomers and a monofunctional control under mechanical force. Tensile specimens were uniaxially stretched (time = 0 min) to achieve a relatively constant true stress after initial relaxation. Absorbance values recorded at the  $\lambda_{\text{max}}$  corresponding to each merocyanine species demonstrate the regioisomer-specific mechanochromism of NP5.

tensile specimens incorporating each naphthopyran molecule were prepared in a similar fashion as the films. The specimens were uniaxially deformed in tension to achieve a relatively constant true stress ranging between 2.4 and 2.8 MPa after initial relaxation. The mechanical stress was maintained during the course of the experiment while visible absorption spectra were recorded every 30 min (see Figure S1). An immediate increase in the absorbance around 440 nm was observed upon mechanical deformation of the PDMS material incorporating

NP5, corresponding to the absorption peak ( $\lambda_{\text{max}}$ ) of the merocyanine species obtained after irradiation with UV light. The absorbance continued to increase asymptotically while the specimen was maintained under mechanical stress. In contrast, the absorption spectra of materials containing the two other naphthopyran regioisomers, NP8 and NP9, did not change over the course of the experiment. The absorption spectrum of the control specimen also did not change under mechanical stress, confirming that mechanical force was indeed responsible for the color change in the material incorporating NP5.

In order to rationalize the regioisomer-specific mechanochemical reactivity of naphthopyran, we evaluated the geometrical constraints imposed on the molecule under mechanical stress. Similar to the lever-arm effect, which originates from more efficient chemomechanical coupling through a properly aligned polymer backbone,<sup>20</sup> we posited that the orientation between the externally applied force and the C–O pyran bond is important for efficient mechanochemical transduction along the reaction coordinate. From the highly constrained molecular structures obtained from CoGEF calculations immediately prior to bond rupture, the angle between the vector of applied tension and the vector representing the C–O pyran bond was calculated for each regioisomer (Figure 4). The vector



**Figure 4.** Geometrical evaluation of constrained naphthopyran structures obtained from CoGEF calculations at displacements immediately prior to bond cleavage. The directionality of the applied force is approximated by the vector between the terminal oxygen atoms ( $\overrightarrow{AB}$ , yellow arrow), while a second vector describes the C–O pyran bond ( $\overrightarrow{CD}$ , red arrow).

representing the applied force was approximated by the coordinates of the methoxy oxygen atoms of the elongated structures (see the SI for details). For the mechanically active naphthopyran regioisomer substituted at the 5-position, the relatively shallow angle of  $31^\circ$  between these two vectors reflects a good alignment of the C–O pyran bond with the directionality of the external force. For the other two naphthopyran regioisomers substituted at the 8- and 9-position, this angle is significantly wider at  $55^\circ$  and  $65^\circ$ , respectively. This trend is consistent with an alternative description of mechanochemical coupling<sup>11</sup> based on the calculated elonga-

tion that accompanies the ring-opening reaction for each regioisomer (see the SI for details).

In summary, we have demonstrated that naphthopyran is a new mechanophore capable of color generation in polymeric materials using mechanical force. Notably, only the naphthopyran regioisomer substituted at the 5-position exhibits mechanochromic behavior, while regioisomers substituted at the 8- and 9-position are mechanochemically inactive. This trend in reactivity was also accurately predicted by DFT calculations (CoGEF). We attribute the mechanochemical activity of the naphthopyran regioisomer substituted at the 5-position to the better alignment of the C–O pyran bond with the direction of the externally applied mechanical force along the reaction coordinate. Further research will investigate the influence of structural modifications to the naphthopyran mechanophore in order to tune the color and control the fading properties.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07610.

Experimental details, synthetic procedures, and NMR and visible absorption spectra (PDF)

Movie showing the color change of NP5 upon stretching a PDMS specimen (MPG)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*jsmoore@illinois.edu

\*n-sottos@illinois.edu

### Notes

The authors declare no competing financial interest.

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