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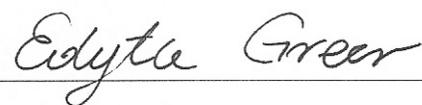
Reflectance Analysis and Thermochromicity of Fabrics Dyed with Indigo, 6-Bromoindigo, and 6,6'-Dibromoindigo

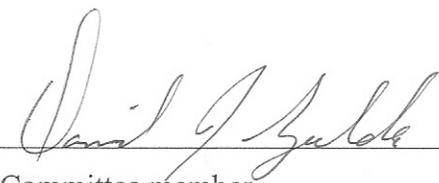
Irina Mironova

Submitted to the Committee on Undergraduate Honors of Baruch College of the City University of New York in partial fulfillment of the requirement for the degree of Bachelor of Arts in Biological Sciences with Honors

Approved by the Department of Natural Sciences:

  
\_\_\_\_\_  
Mentor  
Dr. Keith Ramig

  
\_\_\_\_\_  
Committee member  
Dr. Edyta Greer

  
\_\_\_\_\_  
Committee member  
Dr. David Szalda

Laboratory of Professor Keith Ramig

-April 26, 2013-

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## **Abstract**

This thesis is focused on explaining the thermochromic (color change with heat) properties of fabric dyed with the indigo derivatives 6-bromoindigo (MBI) and 6,6'-dibromoindigo (DBI). MBI- and DBI-dyed textiles change color upon heating from violet to blue and from purple to red, respectively. To quantitatively evaluate changes in fabrics' shades we used reflectance spectra analysis. The technique of shining a beam of light onto the fabric and recording the wavelength of light which was reflected allowed us to objectively record the color transformation. There is no current theory which can predict fabric color based on molecular structure of the dye and fabric; neither is there an explanation for the unique trends in color change upon heating. In order to observe molecular behavior with transmission electron microscopy (TEM), we dyed carbon nanotubes as fabric surrogates. TEM images of dyed nanotubes revealed certain patterns. DBI and MBI molecules form aggregates of particular sizes on the nanotubes, which seem to correspond to particular reflected colors. We believe that change in fabric color after heating is related to the change in size of the aggregates on the nanotubes. Preliminary results show that smaller aggregates reflect blue light and larger aggregates reflect red. Thus, MBI-dyed cloth contains mostly small aggregates alongside some large aggregates to give fabric a violet color; and after heating, large particles are converted to small, thus the color becomes bluer. On the contrary, DBI-dyed material starts off with larger aggregates and a few smaller ones for a purple tone, but after heating we can see more large particles, which parallels with reddening. Understanding interactions between molecules will allow us to manipulate fabric hues. The successful outcome of the project can find broad use in the fashion industry by improving efficiency of textile coloring and bringing unique shades to the market.

## **1. Introduction**

### **1.1. History of indigoids and modern use**

The art of dyeing developed during the Neolithic Era, earlier than 10,000 BC [Barber et al., 1991]. With the emergence of the variety of textiles the craft of dyeing became a common practice; however, the profession of a dyer posed health risks and was not socially favorable since it involved working with toxic or disagreeable substances like urine [Robinson et al., 1969]. Yet the desire to profit on colored textiles drove searches for new shades nature had to offer. Blue dye became available later, during the 4<sup>th</sup> century BC [Bongioanni et al., 2003], since blue is a rare color in nature [Głowacki et al., 2012]. The source of this unique dye became *Indigofera* genus plants, thus the name “indigo” is used to describe a deep blue hue [Waring et al., 1990, Wisniak, 2004]. During the 1600s BC, indigo and its derivatives, 6-bromoindigo (indigo with one bromine atom attached) and 6,6'-dibromoindigo (indigo with two bromine atoms attached), were found in gland secretions of *Murex brandaris* and *trunculus* mollusks. The mixture of these molecules on fabric produced a vibrant purple color [Koren, 2005]. The rare purple-violet shades obtained from these sea snails became the privilege of royalty and was named Tyrian purple or Royal purple thereafter. German chemist Paul Friedländer was the first to discover that 6,6'-dibromoindigo was the main component of Tyrian purple in 1909 [Friedländer, 1909]. As the dyeing industry evolved and technological advancements allowed for commercial manufacturing of organic colorants, indigo, synthesized in laboratory, still remained the main source of blue hues for fabric coloring and blue jeans dyeings.

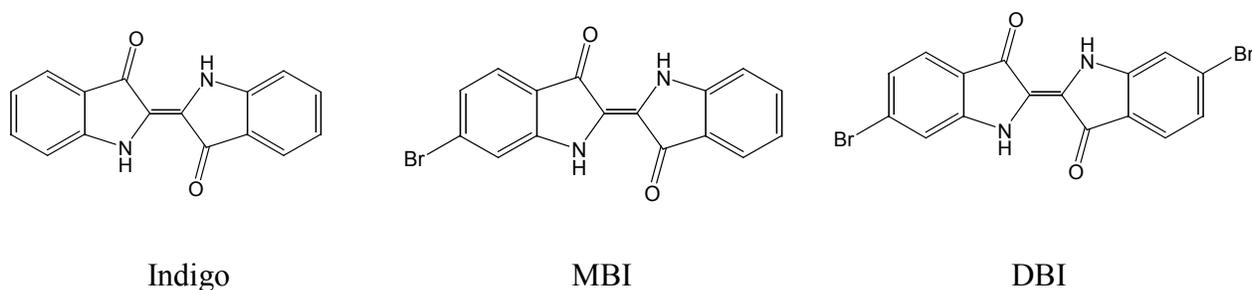
Modern dye manufacturing offers a wide variety of colored fabrics. And with expansion of the fashion industry the demand for new hues and patterns is evolving daily. Purple was named “the reigning color of the season” of autumn/winter 2012-13 by Vogue [The Power of

Purple, 2012]. However, as the seasons change, the designers are urged to find new trends and colors to satisfy the “wandering eyes” of modern fashionistas. We believe that indigo derivatives 6-bromoindigo (monobromoindigo or MBI) and 6,6'-dibromoindigo (dibromoindigo or DBI) could be the new fashion “it”. The intriguing properties of these dyes are the tendencies to change color upon dilution and heating. Strangely enough, indigo itself does not change color upon reduction of dye concentration or boiling. Coloring fabric in a dilute dyeing vat with monobromoindigo or dibromoindigo produces a range of blue shades. Yet during thermochromic (color change with heat) studies, the MBI-dyed fabric turns blue in hot water, while DBI-dyed fabric becomes reddish after similar treatment. As a result, using these dyes, we can produce fabric with hues varying from dark blue to purple-red, which could greatly benefit textile manufacturers worldwide. Moreover, the dynamic property of MBI- and DBI-dyed fabrics could give the consumer more flexibility in choosing a desired shade by simple application of heat.

Currently, there is no clear explanation for the thermochromicity of fabrics dyed with MBI and DBI. Thus, in the course of our research, we investigate the molecular interaction pattern which could account for the thermochromic phenomenon. We suggest that dye molecules form microscopic aggregates on fabric, which determine the visible color. This conclusion was drawn from the reflectance analysis of dyed fabric, where we trace changes in the minima of reflectance curves, and correlate these with changes in the sizes of particles on the microscopic level. Since textile threads were too large for microscopy studies, we used nanotubes (folded carbon sheets) as fabric surrogates. Understanding the types of interactions arising between dye and fabric molecules can allow us to manipulate hues of heated fabrics and learn how to predict a fabric color based on dye structure prior to dyeing.

## 1.2. Dyes and color background

**Figure 1**



Chemical structures of indigoids

The structure of indigo (Figure 1) was proposed by Baeyer in 1883 and confirmed by Von Eller [1955] via X-ray crystallography. And the visible signature blue color of indigo was explained by Christie using Molecular Orbital (MO) theory [Christie, 2007]. We obtained the basis for our dyeing procedure and hints on unique molecular properties of MBI from research of the leading explorers of indigoids: Robin Clark and Christopher Cooksey. These scientists link association of dye molecules into aggregates on fabric with MO explanation of electronic behavior, which accounts for the visible color of MBI-dyed fabric [Clark and Cooksey, 1999].

According to the MO theory [Fukui, 1952], energy required to promote an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) depends on the distance between the orbitals and is mathematically represented by Planck's relationship  $\Delta E = hc/\lambda$  (where  $\Delta E$  is the energy required to promote an electron,  $h$  is Planck's constant,  $c$  is the speed of light and  $\lambda$  is the wavelength of the absorbed light by the electron). The visible-light wavelengths vary from 380 to 750 nm in the electromagnetic spectrum. Red-colored light has long wavelengths and is therefore low in energy, while blue has short wavelengths, and is high in energy (Table 1).

**Table 1**

Wavelength of Maximum Absorption (nm)	Color Absorbed	Color Observed
470-500	Blue-green	Red
500-520	Green	Purple
520-550	Yellow-green	Violet
550-580	Yellow	Violet-blue
580-620	Orange	Blue
620-680	Red	Blue-green

The HOMO-LUMO gap in indigo is relatively small, thus, only low energy red light is required to excite an electron to the higher orbital. As the red light is absorbed the complimentary blue color is reflected and is visible to the viewer. The relatively small HOMO-LUMO gap is due to a particularly stable lowest unoccupied molecular orbital because of the conjugated system of  $\pi$  electrons. The benzene rings'  $\pi$  electrons are connected via a "cross-conjugated" ethene bridge, which also enables communication between two electron donor groups (NH) and two electron acceptor groups (C=O). Such a configuration is referred to as the H-chromophore [Klessinger 1966, Luettker and Klessinger 1964, Luettker et al 1966]. Furthermore, Clark and Cooksey emphasize that hydrogen bonding between dye molecules has an effect on the fabric color. They suggest that indigoid molecules interact with each other so that molecules which are a certain distance from one another, form dimers and higher polymers. The calculated distance between 6,6'-dibromoindigo molecules appears to be smaller than between indigo molecules, possibly because of the van der Waals attraction (a type of intermolecular attraction) between bromine atoms [Clark and Cooksey, 1999]. These stacking patterns supposedly play a role in stabilizing the LUMO, thus affecting the reflected color. Observing the change of fabric hues from indigo (blue) to MBI (violet) to dibromoindigo (purple), it appears that addition of bromine atoms to the indigo molecule destabilizes the LUMO and widens the HOMO-LUMO gap.

There is a physical as well as a chemical explanation for color change. We suggest that visible color of fabric dyed with indigo derivatives could be due to the structural effect. As the observed uneven surfaces or particles (dye aggregates) become extremely small, light waves reflect at different angles producing interference, which in combination with refraction accounts for an iridescence effect. In this case, the surface geometry determines how the light scatters. We suspect that hues appearing on textiles dyed with indigo, MBI and DBI might be explained by structural coloration, as the aggregates we observe by TEM (transmission electron microscopy) are smaller than the wavelengths of the light being shined on them. If the properties of the reflected light depend on the type of aggregation, then we can relate observed fabric color to physical behavior of the dye.

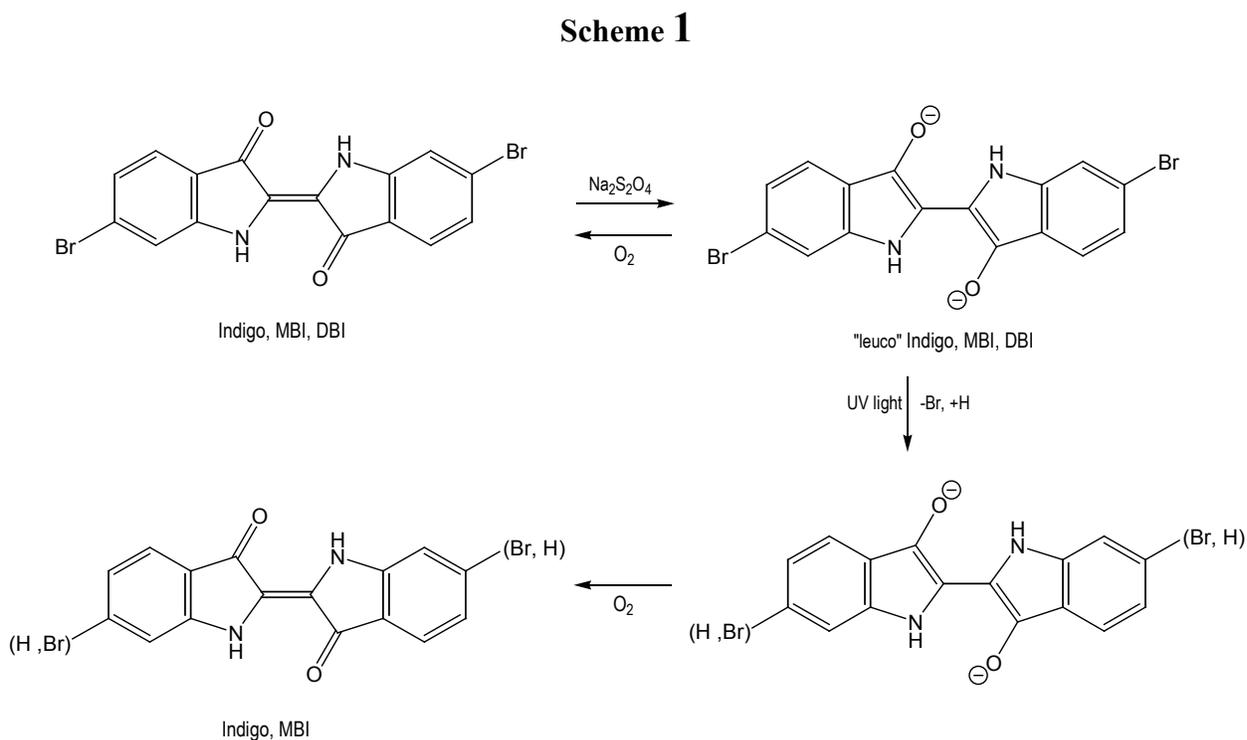
## **2. Results and discussion**

### **2.1. MBI synthesis**

MBI was prepared according to the procedure of Clark and Cooksey [1999]. Although we followed this procedure precisely, our attempts resulted in higher yield than that reported in the paper. During the first two efforts of synthesizing MBI, Baruch student Olga Lavinda and my mentor Dr. Ramig have obtained 55% and 40% yields, which were significantly greater than Cooksey's report of 20%. Dr. Ramig and I have repeated the experiment to confirm a higher yield of MBI (53%). The basis for the discrepancy between Cooksey's and our yields is not known.

## 2.2. Dyeing procedure modification

It is known that indigoids are poorly soluble in water, and for dyeing purposes, they first have to be converted to a water-soluble form called “leuco” or colorless (soluble form of indigoids, Scheme 1). The molecule, in “leuco” form, carries positive and negative charges, which are attracted to the surface of the fabric if it’s polar. The dyeing procedure was employed from Clark and Cooksey [1999] and improved to obtain more consistent results. Later it was found that Cooksey [2005] had modified his original DBI-dyeing procedure so that we matched closely the conditions he used.



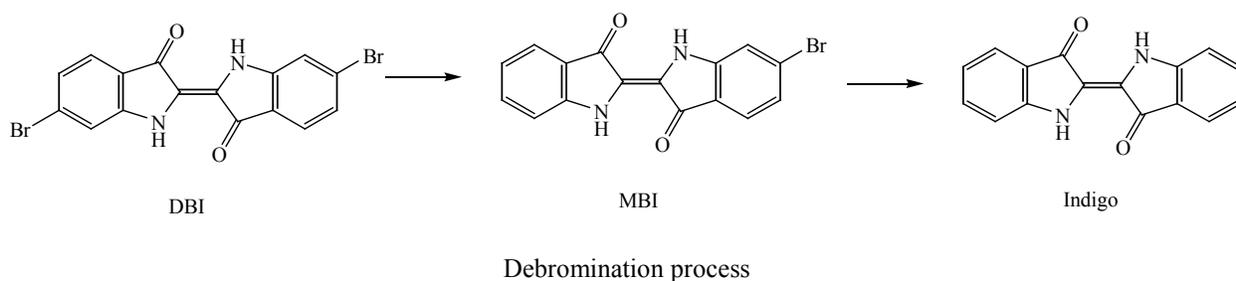
The following steps were taken in the process of modification.

### 2.2.1. Analysis of the influence of UV light

As indicated in the literature during the “leuco” formation, the exposure of the dyeing vat to UV light debrominates indigoids [Van Alphen et al., 1944, Voss et al., 2000, Hoffman et al.,

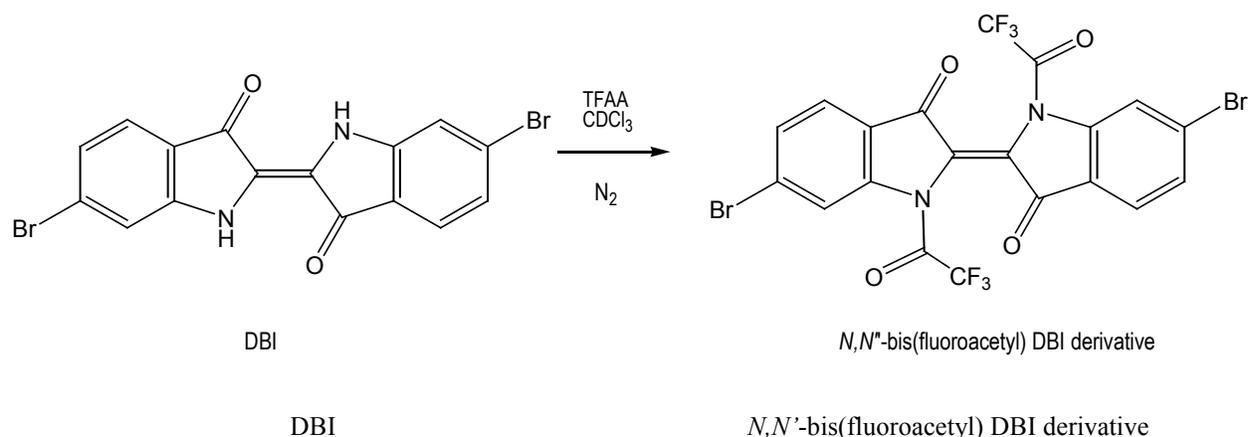
2010 and Driessen, 1944] (Schemes 1 and 2). However, Cooksey and Sinclair [2005] have noted that the leuco form of DBI does not undergo debromination under room lightning. To probe conditions leading to debromination, my mentor with Olga Lavinda, exposed MBI “leuco” to fluorescent light overnight prior to dyeing. Blue-colored fabric indicated loss of the bromine atom from the MBI molecule.

### Scheme 2



To quantify the room-lightning influence, we collected Nuclear Magnetic Resonance (NMR) spectra for indigo, monobromoindigo and dibromoindigo by converting the indigoids to the soluble *N,N'*-bis(trifluoroacetyl) derivative (DBI is shown in Scheme 3) [Gibbs et al, 1995]. The NMR images of indigo, MBI and DBI were used as a reference in room-light-effect investigations (See Appendix A). To observe whether debromination occurs, we converted MBI to “leuco”, and without adding the fabric, we left it to stir under fluorescent light for the time of a three-pass dyeing. Afterward, the “leuco” was exposed to air and reformed insoluble dye particles were suction filtered; plus, the filtrate was evaporated under reduced pressure to recover more dye. The regained dye was prepared for NMR analysis by the trifluoroacetylation reaction mentioned above.

### Scheme 3



MBI and DBI spectra showed a distinct peak in the region from 8.2 to 8.4 ppm, while the indigo spectrum did not show this important feature. Analysis of the MBI sample, which had undergone “leuco” formation under room light, gave inconclusive results. Although, the spectrum had peaks in the region from 8.2 to 8.4 ppm, we could not determine whether debromination occurred on some molecules of the sample. Moreover, we attempted to characterize the processed MBI by  $^{19}\text{F}$  NMR which seemed to be a promising technique (See Appendix B), but as standard samples were collected for indigo, MBI and DBI, an NMR apparatus malfunction prevented us from completing the analysis.

Since we observed that the colored fabric, produced during the time span of a normal dyeing (a few hours) under fluorescent light, showed the same colors as fabric dyed with protection from room lighting, we decided to perform future experiments without protection from light in order to be able to observe closely any color changes or other phenomena that occurred during the dyeing.

### **2.2.2. Temperature effect**

Before I joined the project, Lavinda and Ramig in unpublished results had tested the effect of temperature at which dyeing was carried out, on fabric colors. First, they dyed fabric at room temperature:

#### DBI dyeing at room temperature (22-23 °C)

The dyeing was made at half the scale of the original procedure by my mentor and his research team, where the “leuco” was prepared at 50 °C. Before the fabric was introduced, the flask was cooled down to room temperature. Developed multifabrics cloth had very faint colors, while some fabrics weren’t colored at all. Besides, upon the procedure completion, the dyeing vat was exposed to air to precipitate insoluble dye (Scheme 1). The vat solution turned dark blue, indicating a large amount of residual dye. They concluded that decreasing dyeing temperature yields poor results. As I became a part of the research crew, we repeated 50 °C fabric dyeing, however, this time we increased the temperature at which “leuco” was formed. This is detailed in the following section.

#### DBI-dyeing at 50 °C

The “leuco” was formed at reflux (77-78 °C) and cooled to 50 °C for multi-strip coloring. Dyed fabrics presented faded colors and unevenly distributed dye (Figure 2), and the post-dyeing vat contained many blue particles. Attempts to reproduce this dyeing gave unsatisfactory results, as the colors differed each time, possibly due to the varying amounts of dye on the fabric. We will show in Section 2.4 that the colors of the dyed fabrics depend strongly on the concentration of the dye, in the cases of MBI and DBI.

**Figure 2**

DBI

1<sup>st</sup> pass      2<sup>d</sup> pass      3<sup>d</sup> pass



Multi-fabric strips dyed with DBI at 50 °C

To increase efficiency of coloring, we carried out the entire procedure at elevated temperatures (77-78 °C). This is described below.

Dyeing at reflux with all three dyes (77-78 °C)

The “leuco” formation and dyeing both took place at reflux. We have obtained richly colored fabrics (Figure 3). After the third pass at reflux the vat did not contain any blue particles after exposure to air, indicating optimal dye adherence to the material. Later, we discovered that Cooksey and Sinclair [2005] performed their DBI dyeings at reflux as well; however, unlike in our experiment, they used excess (2 g) dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) reagent and concentrated ammonia solution (7 mL) to convert the dye to “leuco,” diluting the solution with water after. This differs slightly from our procedure (see Experimental Section), but the two procedures would be expected to give the same colors.

**Figure 3**



Indigo (top) vs. MBI vs. DBI (bottom) dyed at reflux  
13 fabrics on each horizontal strip. From l to r: wool, viscose, polypropylene, silk, orlon, nylon, dacron 64, dacron 54, creslan, cotton, triacetate, modacrylic, diacetate.

To obtain consistent results, all dyeings with indigo, MBI, and DBI were carried out under fluorescent room lighting and at the reflux temperature according to the new procedure.

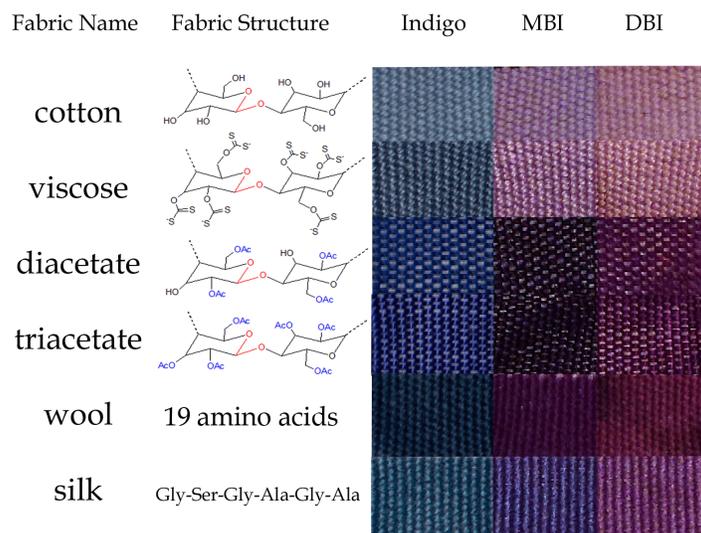
### **2.3. Effect of fabric structure on visible color**

We have conducted a thorough analysis of dyed fabrics to trace how fabric structure influences visible hues. Expecting that materials similar in polarity would display the same shades, we compared fabrics with similar backbones and polarity. It appears that some fabrics exhibit more intense colors than others, and shades of purple and violet vary irrespective of fabric functional groups. This tendency was explained by Cooksey and Sinclair [2005], who suggested that the “leuco” form of indigoids is strongly attracted to a fabric’s polar functional groups by hydrogen-bonding, ionic, polar and nonpolar interactions. As the dye in “leuco”, or charged, form is applied to the fabric, the molecules interact with fabric and with each other. When the indigoids are oxidized back into insoluble form, the attraction between dye molecules prevails over substrate-molecule attraction, creating dye aggregates. Textiles which appear bluer have stronger dye molecule-fabric interaction, while materials with violet hues have more dye aggregates. Nylon has a stronger attraction to dye molecules than wool, thus nylon appears bluer

(Figure 4 and 5). While in wool, the attraction of colorant's molecules to each other is greater and the fabric looks violet. It seems that dye aggregations reflect light in a different manner than single molecules, uniformly distributed over the fabric. As a result, we see redder shades on fabrics with particles and bluer on evenly allocated colorant. While Cooksey and Sinclair do not provide direct evidence of dye aggregation, we confirm dye spatial accumulation by electron microscopy during our study.

Figure 4 illustrates the structural composition of various fabrics. Since indigo-dyed fabrics vary in the intensity rather than the shade of the blue color, we did not focus our attention on indigo-dyed textiles. MBI- and DBI-dyed materials vary in shade from blue to violet and soft pink to bright burgundy respectively. It appears that addition of bromine to the blue indigo molecule tilts fabric hues towards red: monobromoindigo-dyed materials look more violet and dibromoindigo-dyed cloth obtains distinct reddish tones. We can see that cotton, viscose, diacetate and triacetate consist of glucose backbone with polar functional groups, yet color shades vary irrespective of fabric's structural similarity. The separation is more obvious in the next example, where textiles such as wool and silk, which consist of amino acid chains, are colored in remarkably different shades.

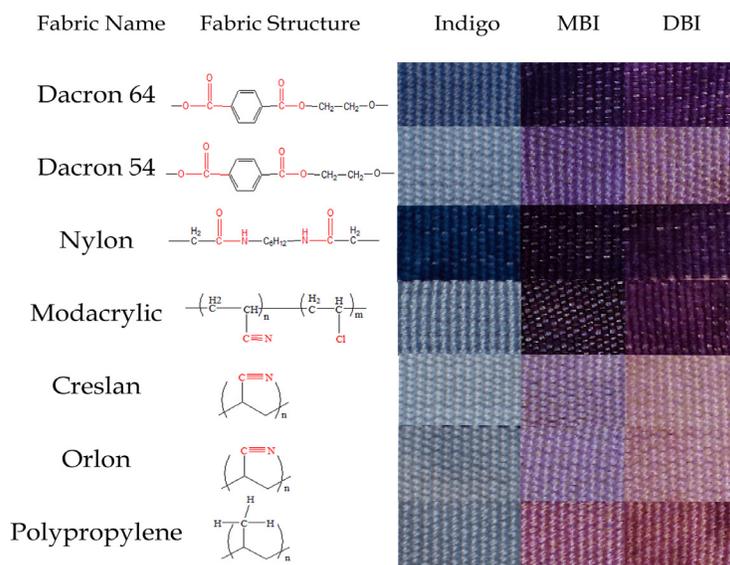
**Figure 4**



Fabrics' structures correlated to the visible colors

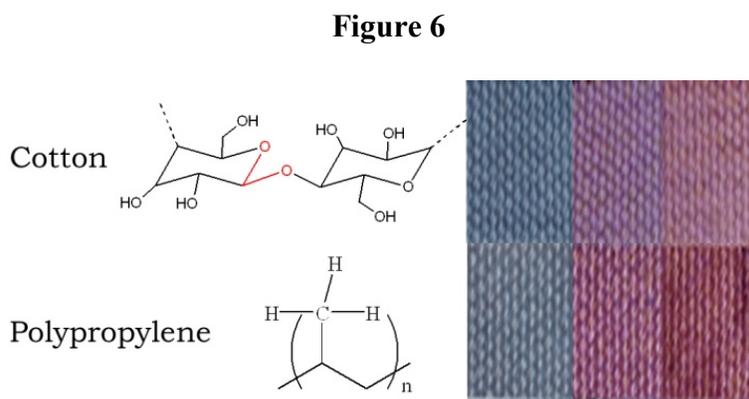
Similar analyses were applied when examining the next set of fabrics (Figure 5). Synthetic textiles with identical functional groups like modacrylic and creslan, containing the nitrile group ( $\text{—C}\equiv\text{N}$ ), express a wide range in color, particularly visible in MBI and DBI dyed fabric.

**Figure 5**



Fabrics' structures correlated to the visible colors

While looking at fabrics exceptionally distinct in structure like cotton and polypropylene side by side, we can mistake one for another after dyeing (Figure 6).



Fabric's structures correlated to the visible colors

From the observations above, we can conclude that visible hues depend mainly on arrangements of dye molecules with respect to each other and not heavily on functional groups of the textiles. This conclusion was reinforced by observations of fabrics after brief boiling in water (Figure 7), where fabrics changed color irrespective of their structural composition. Using an example of fabrics with an amino acid backbone, like wool and silk, we observed that MBI-dyed silk changed color to blue-green, while MBI-dyed wool acquired the deep blue hue. The difference is more prominent in the DBI-dyed cloth, where wool changes to bright red and silk, to soft pink.

**Figure 7**

<b>Fabric</b>	<b>MBI before heating (left) after (right)</b>	<b>DBI before heating (left) after (right)</b>
<b>wool</b>		
<b>viscose</b>		
<b>polypropylene</b>		
<b>silk</b>		
<b>orlon</b>		
<b>nylon</b>		
<b>Dacron 64</b>		
<b>Dacron 54</b>		
<b>creslan</b>		
<b>cotton</b>		
<b>triacetate</b>		
<b>modacrylic</b>		
<b>diacetate</b>		

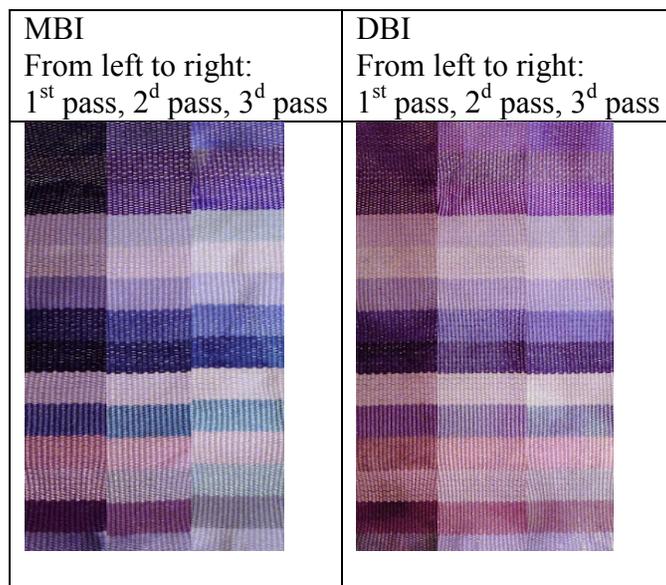
Multi-fabric strips color change upon heating

#### **2.4. Dilution effect**

It has been mentioned in the literature that MBI- and DBI-dyed wool [Koren, 2005] and silk turn blue as the dyeing vat becomes less concentrated with colorant [Cooksey, 2005]. Since indigo-dyed fabric did not show color change, we focused on studying MBI- and DBI-dyed textiles. The proposed explanation of bluing upon dilution is that dye molecules form dimers or higher polymers and undergo self-association to form dye particles [Cooksey 2005] once in a highly concentrated solution. However, when dimers have not been formed, solo molecules of dye adhere to the fabric and reflect the blue light. This theory was formulated in the absence of direct physical evidence of dye aggregation.

To extend the study of color change upon dilution, we have performed a series of experiments on other types of fabrics as well as repeated silk and wool dyeings. During the procedure a cloth of fabric was introduced to the dyeing vat and removed after 15 min which was followed by the next piece of cloth and the third to exhaust the dyeing vat. Each addition of the fabric to the vat is referred as a “pass.” We have found that a standard dyeing vat at reflux sustains three passes. After coloring multi-fabric strips as well as silk and wool cloths separately, we found that material bluing is consistent across all textiles in the 3-pass dyeings. Furthermore, we concluded that bluing occurs irrespective of the dye used: MBI or DBI (Figure 8).

**Figure 8**



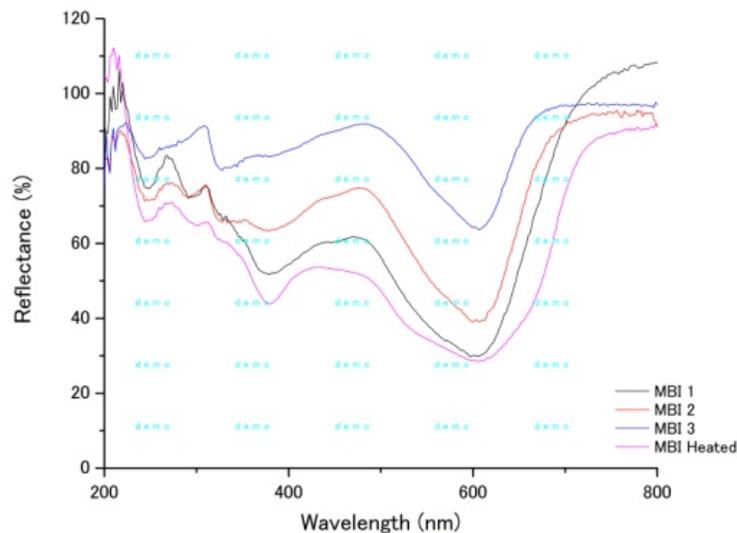
Bluing effect upon dilution

To quantitatively evaluate the bluing effect across passes, our collaborators Hiroko Ajiki from Hunter College and Federica Pozzi from The Metropolitan Museum of Art performed reflectance spectra analysis on all types of fabrics from all three passes. A similar, less extensive study has appeared recently [Koren, 2012]. That study employed fabrics dyed by Ramig and Lavinda, and were used by Koren without their knowledge or consent. The fabrics analyzed had

been prepared by one of the low-temperature inconsistent methods reported in Section 2.2.2. Thus, the conclusions of that study should be regarded with circumspection.

The first pass of the MBI-dyed Orlon (Figure 9, black line, MBI 1) shows a peak at 610 nm and a small shoulder extended in the lower 500s region on the reflectance graph. A minimum in a certain region indicates that most of the light was absorbed and the reflected wavelength is the observed color. In this instance, minimum in the region of 600 nm corresponds to a reflected blue light and extension to 500 nm corresponds to violet (refer to Table 1). The second pass (red line) has a minimum at 600 nm and the shoulder in the 500s is much smaller indicating that we will see less of the red hues. And in the third pass (blue line), the graph is almost symmetrical with a sharp minimum at 610 nm, which is consistent with the observed color: bluing upon dilution.

**Figure 9**

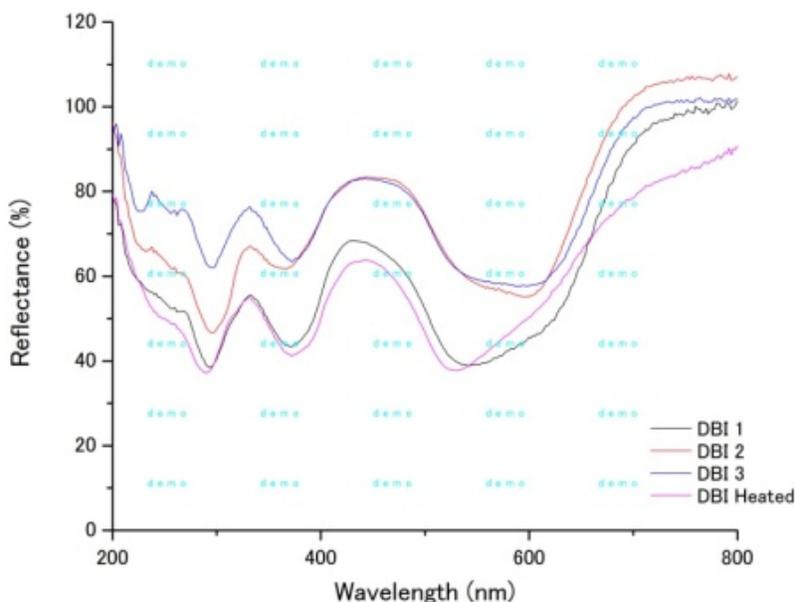


Reflectance spectrum of the MBI-dyed orlon from a multi-fabric strip

MBI 1 – first pass, MBI 2 – second pass, MBI 3 – third pass and MBI heated – boiled fabric

In another example, where DBI-dyed cotton has been analysed (Figure 10), we can find a minimum in the lower 500s with a shoulder extending to the 600s in the first pass (black line, DBI 1) consistent with a violet color. However, in the second pass (red line), the minimum shifted to 600 nm and a shoulder remained in the higher 500s. This valley modification corresponds to a blue change. The third pass (blue line) exhibits a broad minimum in the region from the higher 500s to the lower 600s, agreeing with violet-blue color of the dyed cloth. See Appendix C for the rest of the spectra of the other fabrics.

**Figure 10**



Spectrum of the DBI-dyed cotton from multi-fabric strip  
 DBI 1 – first pass, DBI 2 – second pass, DBI 3 – third pass and DBI heated – boiled fabric

As Cooksey noted, dye molecules form polymeric aggregates on fabric in highly concentrated solution, which affect the reflected color. We suggest that the size and the shape of these aggregations possibly play a key role in visible fabric color. Thus, as less dye is available for polymer formation, molecular aggregates become smaller. Small dye particles seem to be

responsible for the blue color, while larger species reflect light with longer wavelengths in the “red” regions.

## **2.5. Thermochromic studies**

The tendency of MBI-dyed material to change color after boiling, which is referred to as a thermochromic property, has been noted previously [Ziderman, 2004]. We have extended the MBI study to other fabrics and also examined the color change of DBI-dyed fabrics upon heating. Also, we have noted that indigo-dyed textiles did not change color greatly upon heating; therefore, we used indigo dyeings as a control in subsequent studies.

Ziderman [2004] has noted that MBI-dyed wool changes color towards blue when boiled. During our experiments, we found that other fabrics colored with monobromoindigo change hues towards blue when heated in water. However, as proposed by Lavinda and Ramig [Lavinda et al., 2013], the testing of this property on DBI-dyed textiles showed an opposite trend. Contrary to MBI-colored materials, DBI-dyed fabrics turned redder. Such intriguing behavior encouraged further study of thermochromic property of indigoids.

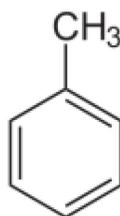
### **2.5.1. Solvent effect**

First, we examined the solvent effect: whether the color change is an inherent property of dye molecules or rather is influenced by surrounding conditions. We heated dyed fabrics by different means: dry heat, boiling in a non-polar solvent, and boiling in water. Ziderman [2004] noted that when dry pure violet MBI is sublimed (solid converted to vapor by application of dry heat) and re-deposited (converted back to solid from vapor), it changes its color to blue. However, Olga Lavinda and Dr. Ramig found on the contrary that crystals of MBI, heated to 200

°C (sublimation temperature of dye) do not change their color [Lavinda et al., 2013]. A relationship between the color change of sublimed and re-deposited dye crystals (if that color change can be verified) and fabric color changes, which occur even as low as 60 °C in water, is unlikely, given the extreme temperature differences. To study the dry heat effect further, we inserted MBI-dyed wool into a heating oven at 100 °C overnight. The wool strip of cloth did not show any color change. In addition, we observed unusual bluing of MBI- and DBI-dyed fabric when placed onto a hot plate at 250 °C. We suspect that extreme temperatures decomposed the dye molecules as well as the fabric, causing appearance of a bright blue color.

Next, the wool dyed with monobromoindigo was boiled in the non-polar solvent toluene (Figure 11) for 15 minutes. It appeared that this solvent partly removed dye from the fabric, as evidenced by a violet coloring of the solvent, but did not change the shade of the cloth.

**Figure 11**



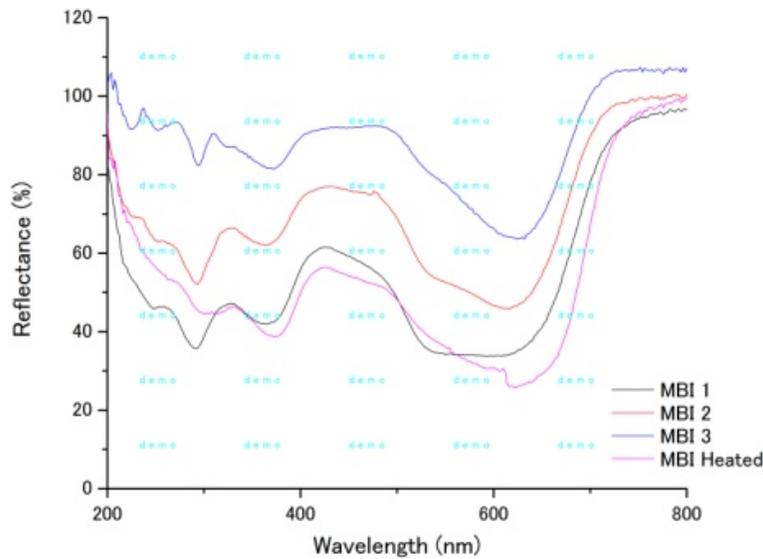
Toluene

However, when the fabric was boiled in water, in which the dye is completely insoluble, we could clearly observe the color change and none of the dye was removed from the fabric. Thus, from the solvent observations, we conclude that water plays an integral role in expressing the thermochromic properties of MBI- and DBI-dyed materials, but color change is not an effect of solvation of the dye molecules.

### 2.5.2. Analysis of dyed, heated multi-fabric strips

In the course of heating different fabrics, we tested the significance of time of water contact with the fabric. MBI-and DBI-dyed silk placed in hot water for 15 seconds and 10 minutes did not show any difference in their shades. As stated above, the heated MBI-dyed multi-fabric strips turn bluer, while heated DBI-dyed multi-fabric strips turn redder (Figure 7). Turning to the other fabrics, it is evident from the MBI-dyed cotton reflectance spectra that the first pass (black graph) has an absorption maximum at 540 nm with a large shoulder in the mid-600s, which accounts for the violet (red + blue) shade, but the first pass after heating (pink graph) showed different values: minimum shifted to the lower 600s and a small shoulder remained in the upper 500s, indicating fabric bluing (Figure 12).

**Figure 12**



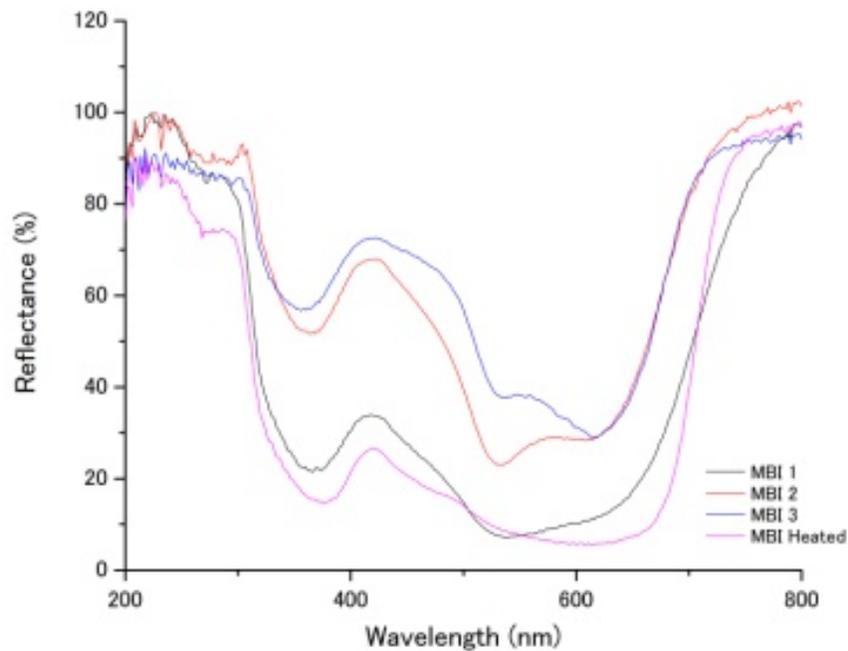
Spectrum of the MBI-dyed cotton from multi-fabric strip  
MBI 1 – first pass, MBI 2 – second pass, MBI 3 – third pass and MBI heated – boiled fabric

Proceeding to DBI-dyed cotton spectra we can observe different behavior (Figure10): the first pass (black line) had a minimum at 510 nm and a long shoulder in the lower 600 nm range,

while the graph for the heated first pass (pink line) obtained a more symmetrical shape with a minimum at 510 nm. This valley shift implies the change of fabric color from lilac to purple-red.

To follow up on Ziderman's MBI-dyed wool experiments, we closely analyzed wool dyed with MBI and DBI. The first-pass spectrum of the MBI-dyed wool (Figure 13, black graph) displayed a minimum at 530 nm and a long extension to the middle 600s, corresponding to the violet color. After heating, the first pass of wool turned dark blue and the reflectance graph changed in shape accordingly (pink line): a deep protuberance in the lower 600s which broadly extends to the upper 500s.

**Figure 13**

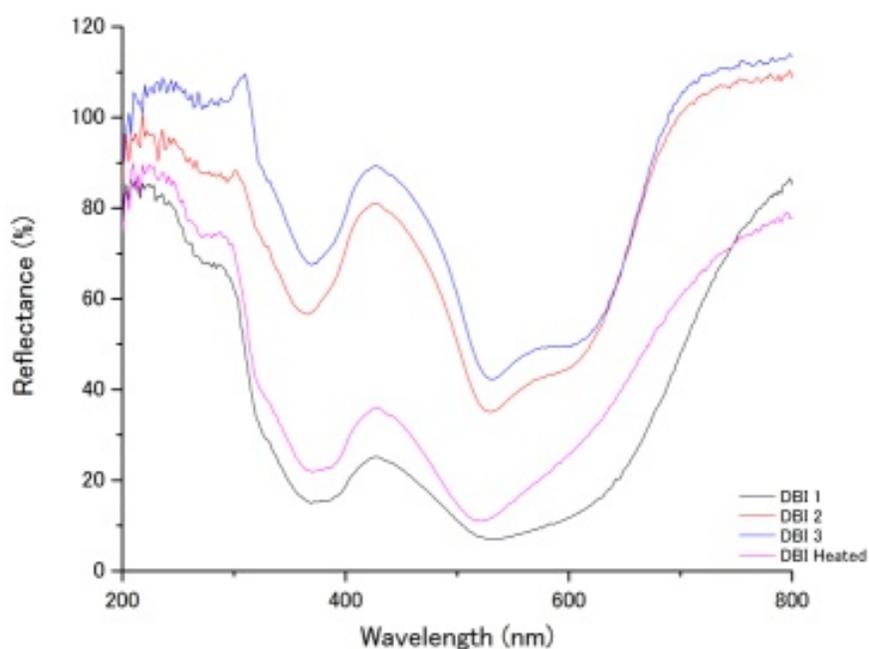


Spectrum of the MBI-dyed wool from multi-fabric strip  
MBI 1 – first pass, MBI 2 – second pass, MBI 3 – third pass and MBI heated – boiled fabric

Moving on to the first-pass spectrum of the DBI-dyed wool (Figure 14, black line), we can observe that the graph greatly resembles the first-pass spectrum of the MBI-dyed wool

(Figure 13, black line). However, the spectrum of heated DBI-dyed wool (Figure 14, pink line) exhibits a reverse shift in valley from boiled MBI-dyed wool: the minimum migrated to 520 nm and lost its “blue” shoulder. The contrasting valley-shifts parallel the fabric color change: MBI-dyed wool changed to blue and DBI-dyed wool changed to red.

**Figure 14**



Spectrum of the DBI-dyed wool from multi-fabric strip  
DBI 1 – first pass, DBI 2 – second pass, DBI 3 – third pass and DBI heated – boiled fabric

These trends are representative of all the dyed fabrics. The spectra for the others can be found in Appendix C.

### 2.5.3. Analysis of dyed silk

Lastly, we performed all-silk dyeings where the trends were the most noticeable to the naked eye (Figure 15).

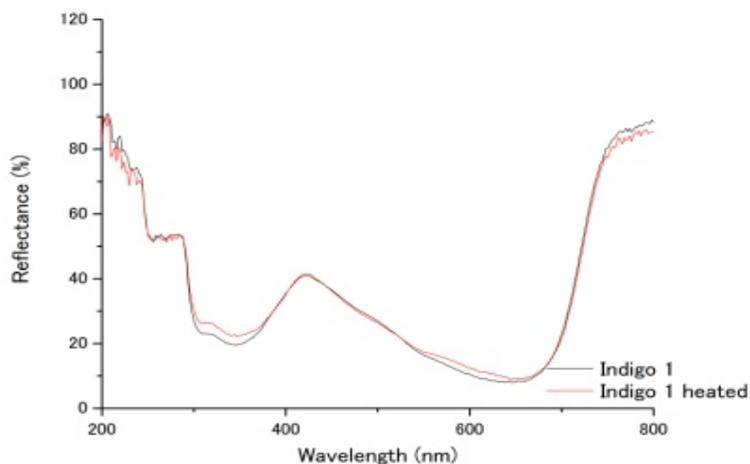
**Figure 15**



Three-pass silk dyeing with indigo (left column), MBI, (middle column), and DBI (right column). Top to bottom: 1st, 2nd, 3rd passes; insets are heated.

Returning to indigo, we can see that the indigo-dyed first pass cloth did not change color markedly after boiling. Looking at the indigo reflectance spectra (Figure 16), we can see that the graphs of non-boiled textile (black line) and boiled (red line) practically overlap, representing no change in visible color. Since indigo does not show any thermochromic properties we did not analyze it further.

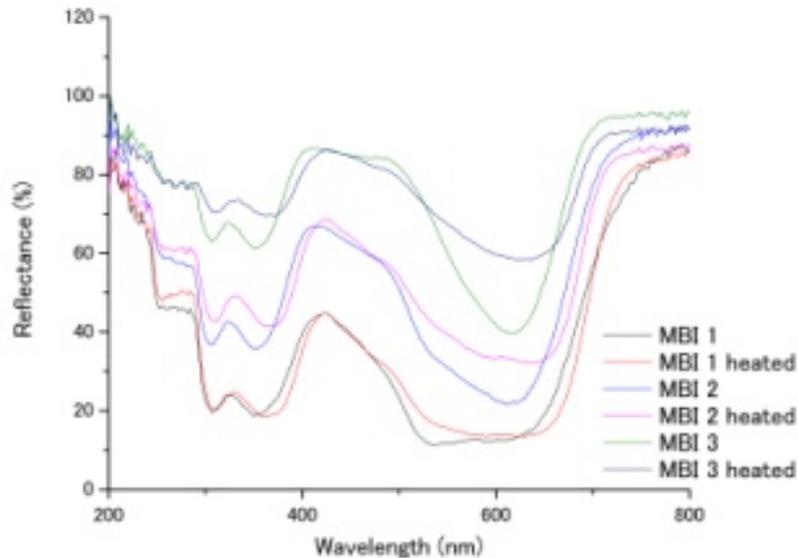
**Figure 16**



Spectrum of the indigo-dyed silk  
Indigo 1 - first pass and Indigo 1 heated – boiled fabric

The first pass of the MBI-dyed silk shows a rich violet color and correlated with the black graph (Figure 17), where the minimum is at 520 nm and a broad shoulder is in the lower 600s. But the boiled first pass (red line) demonstrates diminished extension in the 500s and heavier graph augmentation in the middle 600s. The “red” to “blue” shift is even more prominent on the spectra of the second pass (unheated MBI-dyed silk’s second pass – blue line, heated – purple line), where the valley of the second pass before heating moved to the region of longer wavelengths, after the material was heated.

**Figure 17**

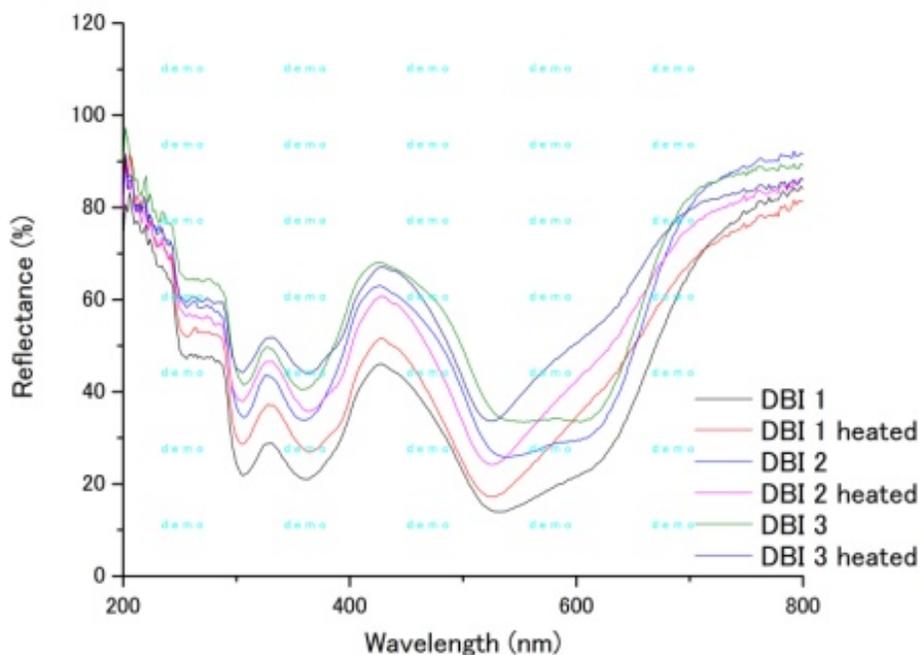


Spectrum of the MBI-dyed silk

MBI 1 – first pass, MBI 1 heated – first pass boiled, MBI 2 – second pass, MBI 2 heated – second pass boiled and MBI 3 – third pass, MBI 3 heated – third pass boiled

In the spectra of the DBI-dyed silks (Figure 18) we can see a minimum of the first pass at 530 nm (black line) and a clear shoulder at 610 nm, yet after boiling, the shoulder disappears and the graph looks symmetrical (red line), indicating loss of silk’s blue shade.

**Figure 18**



Spectrum of the DBI-dyed silk

DBI 1 – first pass, DBI 1 heated – first pass boiled, DBI 2 – second pass, DBI 2 heated – second pass boiled and DBI 3 – third pass, DBI 3 heated – third pass boiled

#### **2.5.4. MBI/DBI mixed dyeings**

To compare which dye adheres stronger to fabric, and is prevalent during the thermochromic studies, we carried out a mixed dyeing experiment, where monobromoindigo and dibromoindigo were blended in equimolar amounts for multi-fabric strip coloring (Figure 19). It appears that for some fabrics DBI is dominant, like wool, viscose, polypropylene and cotton; which appear purple, while for others, MBI: nylon and dacron 64, which look more violet-blue and the rest were an intermediate of the two dyes: silk, orlon, dacron 54, creslan, triacetate, modacrylic and diacetate: variations of purple-violet color.

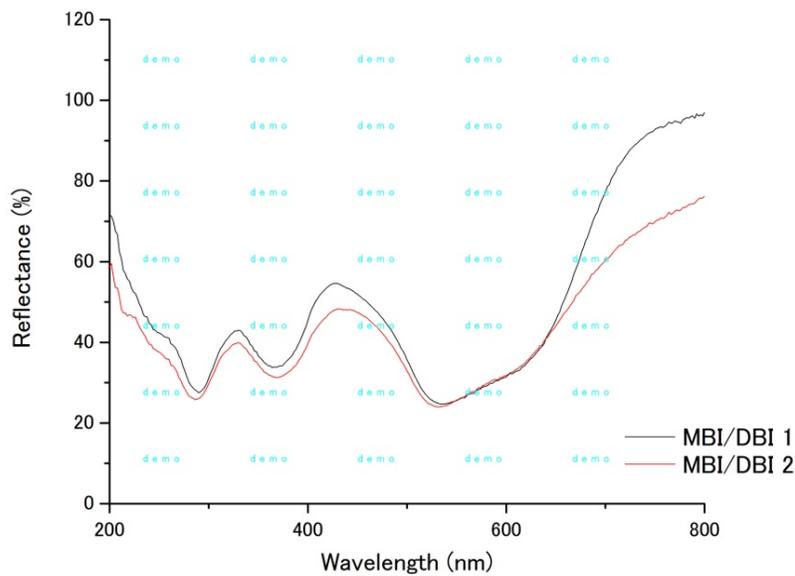
**Figure 19**



MBI-dyed multi-fabric strip (top), hybrid multi-fabric strip (middle) and DBI-dyed multi-fabric strip (bottom).

To examine whether fabric turns redder, because of the DBI, or bluer, because of the MBI, after boiling, we've collected reflectance data for all fabrics before and after boiling. Most of the textiles remained unchanged like cotton (Figure 20), where the reflectance curve before heating (black line) retained its shape after heating (red line).

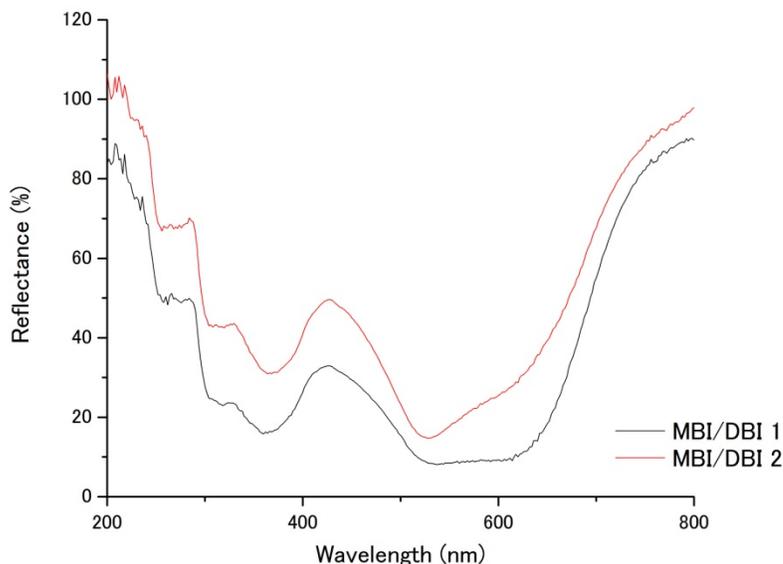
**Figure 20**



MBI/DBI 1 – first pass of cotton dyed with MBI/DBI mixture and MBI/DBI 2 – boiled first pass of cotton dyed with MBI/DBI mixture

Some fabrics turned slightly redder, like silk (Figure 21). In the spectrum of MBI/DBI-dyed silk before heating, we can observe a wide valley in the region from 540 nm to 625 nm (black line) corresponding to blue-violet color. But after boiling, we can see a distinct minimum at 520 nm with a small shoulder at 600 nm, which indicated fabric's reddening.

**Figure 21**



MBI/DBI 1 – first pass of silk dyed with MBI/DBI mixture and MBI/DBI 2 – boiled first pass of silk dyed with MBI/DBI mixture

It appears that for many of these “hybrid” MBI/DBI-dyed fabrics, the blue thermochromic effect of MBI and the red thermochromic effect of DBI cancel each other out. Other fabrics behave more as if they had been dyed with one or the other dye alone. The other spectra of the hybrid dyeings can be found in Appendix C.

### **2.5.5. Capturing color in the process of change**

In order to develop a theory of the color changes caused by heat, we decided to look into the intermediate state of the thermochromic change. We performed an experiment where we

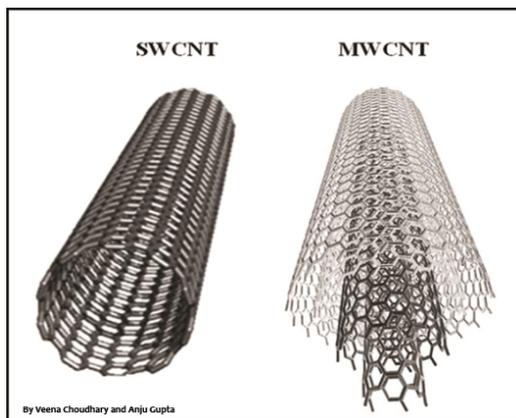
heated MBI- and DBI-dyed fabrics at 40 °C, 60 °C, 80 °C, and 100 °C. Surprisingly, heated MBI-dyed silk presented an unusual pattern: it became slightly redder at 40 °C and more so at 80 °C, yet it turned bluer at 100 °C. Heated at varying temperatures, DBI-dyed silk did not show anomalies. In that case, the color gradually reddened from 40 °C to a final violet-red shade at 100 °C. When a similar test was done on MBI-dyed wool, the reddish intermediate was not present. We plan to examine this irregularity using transmission electron microscopy (see Section 2.6).

From the collected spectral data and a hint from the literature [Cooksey, 2005] we suspected that visible color is determined by the presence of distinct types of molecular aggregates; where aggregates smaller in diameter reflect blue light and those larger in diameter reflect red. Thus, when we detect a color shift from violet to blue for MBI-dyed fabric and from purple to red for DBI-dyed fabric, we expect to observe redistribution of dye molecules from larger particles to smaller in case of MBI and from smaller to bigger in DBI-dyed cloth. In other words, as MBI-dyed textile gets heated, particles reflecting red color are transformed into blue-reflecting ones, and the fabric appears less red (more blue), while boiled DBI-colored material acquires larger clusters of dye molecules and appears less blue (more red).

To support the above statement, we formed a collaboration with Dr. Jacopo Samson of Hunter College, who attempted to examine dyed textile fibers using transmission electron microscopy (TEM), a microscopy technique where a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through and forming an image. Since fabric threads were too big for TEM analysis Dr. Samson suggested carbon nanotubes as an alternative. Carbon nanotubes are large sheaths of interconnected carbon atoms folded into a

tubular shape (Figure 22), resembling material fibers on a much smaller scale, and therefore seemed to be a suitable candidate for dyeings.

**Figure 22**



Single-walled (left) and Multi-walled (right) carbon nanotubes

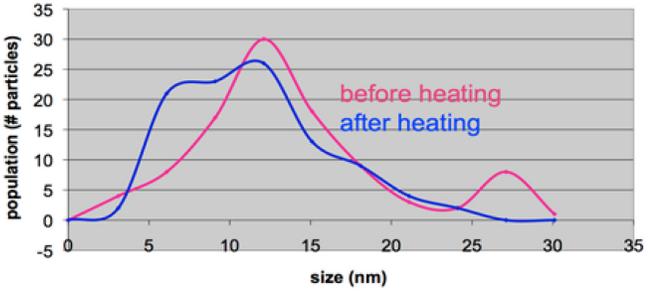
## **2.6. Nanotube dyeings**

### **2.6.1. Single-walled nanotube dyeings**

Usage of carbon nanotubes as fabric surrogates was proposed by our collaborator from Hunter College, Dr. Samson, who carried out the TEM analysis. The tubes appear black to the naked eye and the color change is not visible. Alternative to nanotubes, we attempted to dye silica gel, which consists of white solid beads. Presumably, white silica beads would exhibit a color change when dyed and heated; however, dye molecules did not adhere to the silica surface and further experimentation with silica gel was abandoned.

The first nanotube dyeing with MBI was carried out by Lavinda and Ramig [Lavinda et al., 2013] at 50 °C, according to Clark and Cooksey's original procedure for fabric dyeing [Clark, 1999]. Collected TEM images (Table 2) were analyzed with computer software Image J. Obtained data consisted of distribution of dye aggregates sorted by diameter.

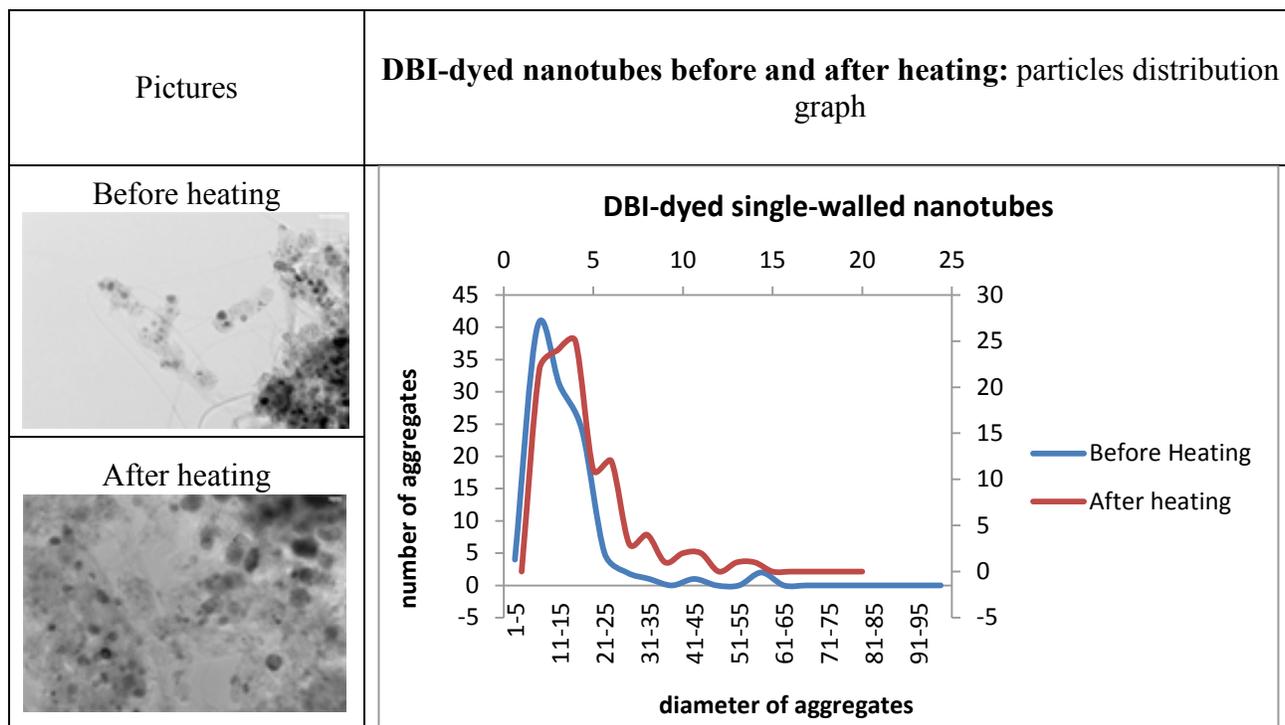
**Table 2**

Pictures	MBI particles distribution graphs																					
	<p data-bbox="841 499 1356 525"><b>Size distribution of mBI-NPs before &amp; after heating</b></p>  <table border="1" data-bbox="755 577 1404 871"><caption>Approximate data from the size distribution graph</caption><thead><tr><th>Size (nm)</th><th>Population (# particles) - before heating</th><th>Population (# particles) - after heating</th></tr></thead><tbody><tr><td>0</td><td>0</td><td>0</td></tr><tr><td>5</td><td>5</td><td>5</td></tr><tr><td>7</td><td>10</td><td>20</td></tr><tr><td>13</td><td>25</td><td>30</td></tr><tr><td>27</td><td>10</td><td>0</td></tr><tr><td>30</td><td>0</td><td>0</td></tr></tbody></table>	Size (nm)	Population (# particles) - before heating	Population (# particles) - after heating	0	0	0	5	5	5	7	10	20	13	25	30	27	10	0	30	0	0
Size (nm)	Population (# particles) - before heating	Population (# particles) - after heating																				
0	0	0																				
5	5	5																				
7	10	20																				
13	25	30																				
27	10	0																				
30	0	0																				

From the graph “before heating” we can see a maximum at 13 nm and a supplementary peak at 27 nm, meaning that the dye particles were predominantly of 13 nm and a good amount of 27 nm in diameter. However, after heating the graph changed its shape: the peak at 27 nm has disappeared and a shoulder in the region of 7 nm has emerged. Correlating the MBI-dyed nanotubes data with the fabric color shift, we found that as MBI-dyed fabric changes color from violet to blue after heating, the distribution of particles changes as well: larger aggregates disappear and smaller ones arise. The observation of particles’ rearrangement suggested that particles of 13 nm in diameter reflect blue light, while particles of 27 nm in diameter reflect red light. As I started to work on the project, we performed a follow up on the first experiment with nanotubes, a DBI dyeing. We predicted that before heating, images of DBI-dyed nanotubes would exhibit predominantly small particles matching the bluish color, but after boiling, we will observe aggregates larger in diameter, related to the fabric reddening. The DBI-dyed nanotubes’ graph confirmed our expectations. We found that non-heated DBI-dyed nanotubes showed most

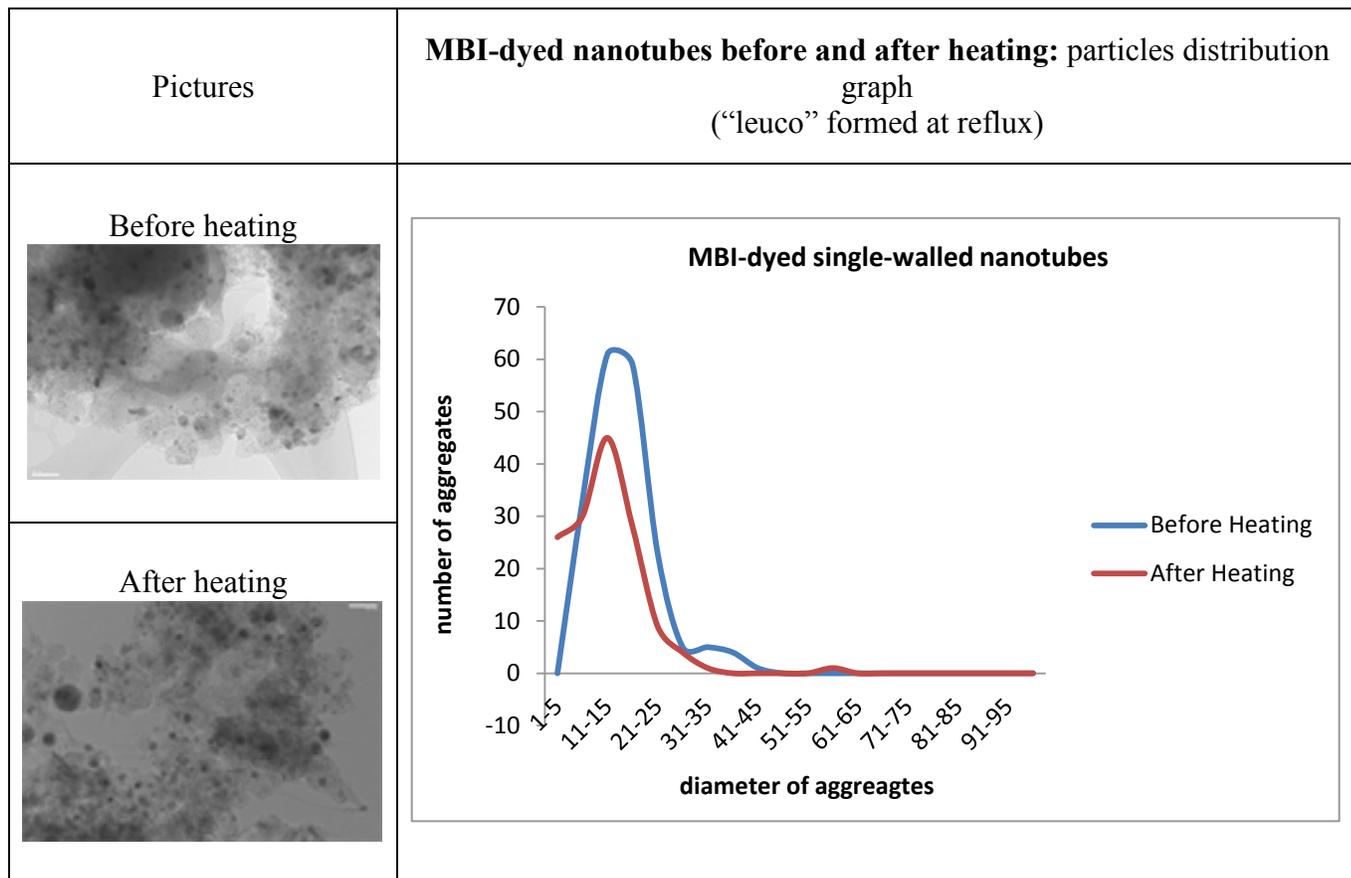
particles with diameter 10-11 nm and after heating, we observed more relatively larger aggregates (30, 40 and 50 nm, Table 3).

**Table 3**



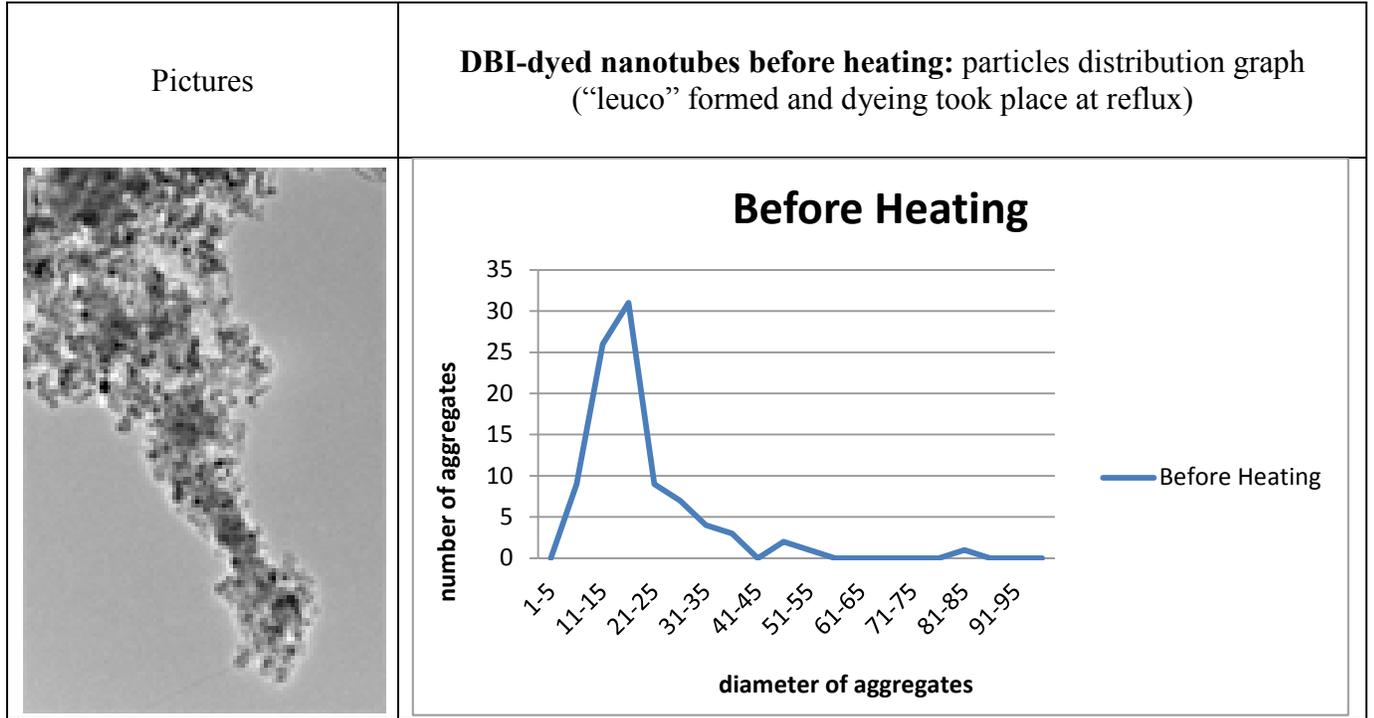
To strengthen preliminary conclusions, we repeated an experiment with MBI, where tubes were dyed at 50 °C, but “leuco” was formed at 77 °C. “Before heating” MBI aggregates were predominantly 15 nm in diameter with slightly increased amount of particles with 35 nm in diameter (Table 4). But after heating, the particles with 35 nm in diameter vanished. The results were consistent with the first nanotubes experiment.

**Table 4**

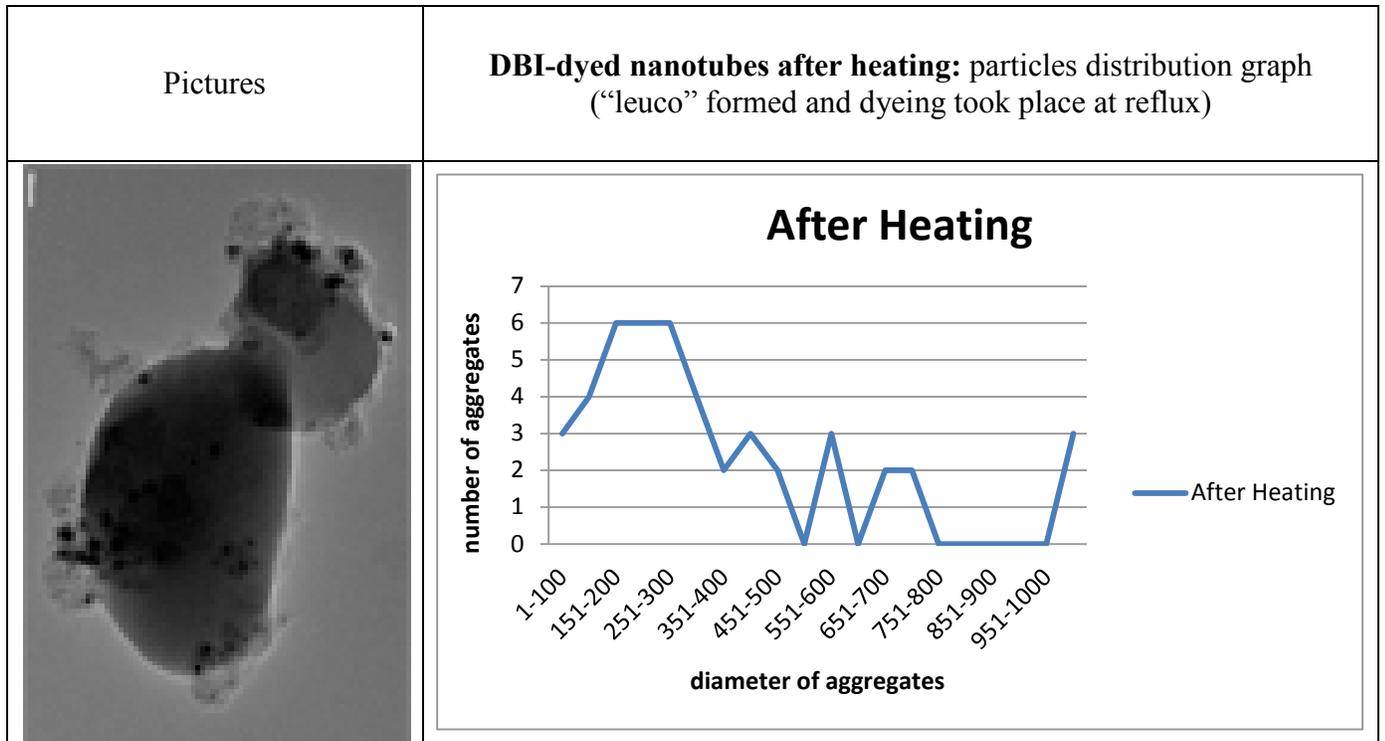


The next nanotube dyeing was performed at reflux with DBI dye. The images of nanotubes before heating contained many particles with 20 nm in diameter (Table 5), which appeared to be consistent with the first DBI-dyeing; however, after heating, the images showed abnormally large particles with diameters from 100 to 700 nm (Table 6). To explain the anomaly of the oversized aggregates, we repeated the experiment with multi-walled nanotubes.

**Table 5**



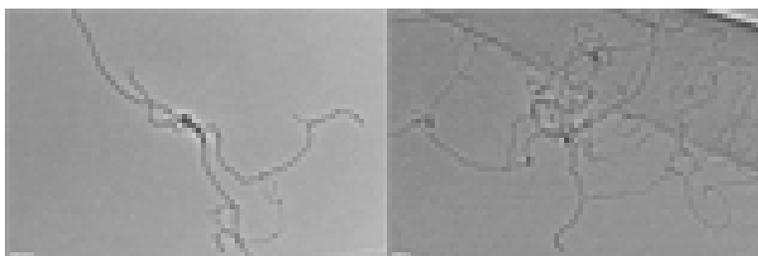
**Table 6**



### 2.6.2. Multi-walled nanotube dyeings

For the next set of experiments we used multi-walled nanotubes because their purity (>98%) was significantly higher than of the single-walled tubes (40-60%), meaning that half of the single-walled nanotubes consist of carbon in random form. As a control, we analyzed pure multi-walled nanotubes with TEM, to ensure absence of any particles on the tubes (Figure 23). The images showed many stringy tubular structures (nanotubes) without any black spots.

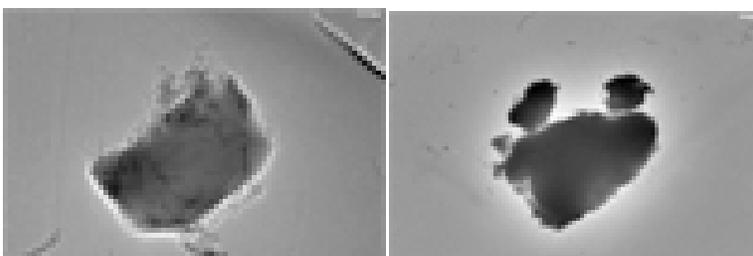
**Figure 23**



Multi-walled nanotubes under the microscope

When we analyzed images of non-boiled MBI-dyed tubes, we found the same irregularity as in the previously mentioned heated DBI-dyed sample of single-walled tubes. We saw large particles with diameters on the micrometer scale and some nanotubes embedded in the much larger globs of dye (Figure 24).

**Figure 24**



DBI-dyed multi-walled nanotubes

We have no explanation currently for the appearance of extremely large dye aggregates. In an attempt to avoid this, we carried out diluted nanotube dyeings in which we removed 2 mL of “leuco” from the vat after we processed the first pass of fabric. Dye particle distribution of the “dilute” nanotubes sample is yet to be determined. Furthermore, we prepared the following samples of the nanotubes, which remain to be analyzed by TEM:

- DBI-dyed multi-walled tubes
- Indigo-dyed nanotubes
- MBI-dyed tubes heated at 40 °C, 60 °C, 80 °C and 100 °C
- Simulated nanotubes dyeing without any dye (a control experiment)
- Dilute indigo dyeing: after the first pass
- Dilute DBI dyeing: after the first pass
- Dilute MBI dyeing: after the second pass
- Double MBI concentration dyeing: after the first pass
- Double MBI concentration dyeing: after the second pass

### **3. Conclusion**

We have examined unexplained properties of the natural dyes, monobromoindigo and dibromoindigo, which were used during ancient times. We have concluded that dyeing with indigoids at higher temperatures gives richer fabric colors and that short exposure of the dyeing vat to fluorescent room light doesn't affect the final hues. Thus, we performed our experiments using modified dyeing procedure: at reflux and without protection from room lighting. Studying color dependence on fabric structure suggested that the visible color of fabric dyed with MBI or DBI is mainly a consequence of dye-dye molecular aggregations, rather than dye-fabric

interactions. Furthermore, we examined the color behavior upon dilution, and upon heating of the fabric. Correlating our findings from the reflectance spectra of dyed fabrics and nanotubes analysis, we believe that dye molecules aggregate on textiles into particles of specific size, which accounts for the observed color. Reflectance analysis showed minima shift corresponding to the change in color. Each subsequent pass of MBI- and DBI-dyed textiles displayed minima shift to longer wavelengths indicating fabric's bluing. While during the thermochromic studies, we found that spectra of the MBI-dyed cloth displayed minima change from shorter wavelength to longer and spectra for DBI-dyed material showed minima shift from longer wavelength to shorter ones. We correlated these observations with TEM images of dyed nanotubes. Evident from the change in the particles' size on nanotubes upon dilution and heating, we predict that larger aggregates reflect red color and smaller ones reflect blue. To probe this further, we need to complete the analysis of dyed nanotubes under different conditions and look into anomalies like MBI-dyed silk's reddening at 40°C, 60°C and 80°C.

#### **4. Future work**

To obtain clear support for our hypothesis that color depends on molecular aggregation, a number of experiments can be performed. The nanotubes studies should be continued until a consistent trend in molecular aggregation is found. Furthermore, since nanotubes appear black to the naked eye, the dyeings should be carried out with a substance which will exhibit a visible color change and will be small enough for TEM analysis. The reflectance study and TEM scanning of one substance will provide strong evidence for or against color dependence on dye aggregation state.

## **5. Experimental**

### **5.1. Chemicals and materials**

DBI was provided by Dr. Sasan Karimi of Queensborough Community College. It was synthesized according to the procedure of Tanoue [Tanoue, 2001]. The DBI purity judged by HPLC peak area is 98%. MBI was synthesized in our lab according to the Clark and Cooksey procedure [Clark and Cooksey, 1999]. MBI was found by HPLC analysis to be 93% pure.

Chemicals obtained from Aldrich:

Indigo (95% pure), CDCl<sub>3</sub> (99.8 % D), trifluoroacetic anhydride ( $\geq 99\%$ ), tetrahydrofuran ( $\geq 99.9\%$ , inhibitor-free), sodium hydrosulfite (sodium dithionite; technical grade, 85%), Benzoyl chloride (99% pure), Toluene ( $\geq 99.5\%$  pure), ethyl benzoate ( $\geq 99\%$  pure), ethanol ( $\geq 99.5\%$  pure), phosphorous pentachloride, single-walled carbon nanotubes (40-60 wt % carbon basis, DxL 210 nm  $\times$  1-5  $\mu\text{m}$ , bundle dimensions) and multi-walled carbon nanotubes ( $>98\%$  carbon basis, DxL, 6-13 nm  $\times$  5-20  $\mu\text{m}$ , bundle dimensions).

Chemicals obtained from Fisher Scientific:

NaOH (98.1% assay), ammonium chloride (99.03% pure).

6-Bromoisatin was obtained from TCI and 3-indoxyl acetate (97% pure) from Alfa Aesar.

The 13 fabrics used in the dyeing were obtained as multi-fabric strips (style # 43) from Testfabrics, Inc.

### **5.2. Instrumentation**

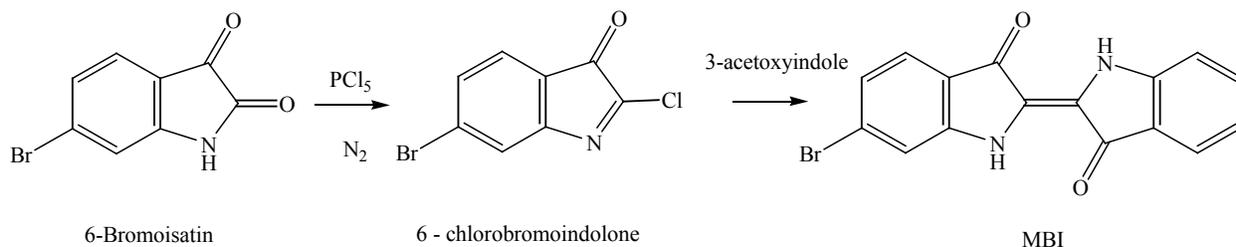
TEM data were collected at 200 kV on a Jeol 2100 instrument equipped with EDAX at the eucentric height to ensure reproducibility of measurements.

Visible reflectance spectra were obtained in dual-beam mode using a Varian Cary 50 Bio UV-Vis spectrophotometer equipped with a Barreliro remote diffuse reflection probe by Harrick Scientific and a xenon flash lamp. The scan range was 200-800 nm with a maximum scan rate of 120 nm/s. Spectra of undyed fabrics were taken before each measurement and used as a calibration reference. The data were processed using Cary WinUV and Origin softwares.

NMR spectra were obtained at 90 MHz in CDCl<sub>3</sub> using TMS as reference.

### 5.3. MBI synthesis procedure (see [Clark, 1999])

**Scheme 4**



A mixture of 6-bromoisatin (1.0 g, 4.4 mmol) and PCl<sub>5</sub> (1.0 g, 4.8 mmol) in chlorobenzene (30 mL) was flushed with N<sub>2</sub> in a flame-dried 3-neck round-bottom flask, and was heated under N<sub>2</sub> at 96-102 °C for 4 hours (Scheme 4). During the heating, the reaction mixture changed color from yellow to red-brown. The mixture was cooled to r.t. and 3-acetoxyindole (736 mg, 4.2 mmol) was added. The solution was left to stand overnight. It was then diluted with ethanol (30 mL) and suction filtered, washing the wine-red solid with ethanol (2x30 mL). A recrystallization from ethyl benzoate (100 mL) was performed under N<sub>2</sub>. The mixture was heated at reflux, although complete dissolution could not be confirmed due to the very dark color of the mixture. A dark-violet powder with a metallic luster crystallized upon

cooling. Suction filtration, washing with ethanol (2x30mL), resulted in 1.52 g (53% yield) of product.

#### **5.4. Indigoids preparation for NMR analysis**

To characterize indigo, MBI and DBI by Nuclear Magnetic Resonance (NMR) we converted indigoids into the soluble *N,N'*-bis(trifluoroacetyl) derivative [Gibbs et al., 1995]. The refluxing apparatus was assembled with dry 10 mL pear-shaped flask under N<sub>2</sub>. MBI (63 mg) was mixed with dry CDCl<sub>3</sub> (2 mL) and trifluoroacetic anhydride (2 mL), and the mixture turned blue. After 30 minutes at reflux the solution turned wine-red color and was cooled for NMR analysis.

#### **5.5. Dyeing procedure**

The dyeing procedure of Clark and Cooksey [1999] was modified. The dyeing is performed in a 250-mL round-bottom flask assembled with a water condenser and swept with nitrogen gas throughout the entire experiment. A solution of distilled water (100 mL), THF (15 mL), and NaOH (0.50 g, 13 mmol) is brought to reflux (75-80 °C) and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (0.50 g, 85% purity, 2.4 mmol) is added, followed immediately by finely ground dye (0.050 mmol). A clear yellow to yellow-green solution forms, indicating formation of “leuco” (Scheme 1). After 15 min, NH<sub>4</sub>Cl (2 g) is added, followed by 1.4 g of fabric which had been soaked in dilute soap solution. The fabric is stirred in the mixture for 15 min then removed and exposed to air to develop the color for 30 min. Lastly, the strip of cloth is washed in 1% acetic acid solution. This constitutes a first-pass dyeing. Another strip of material (1.4 g) is introduced to the vat (second pass) and developed as before, followed by third piece of fabric (third pass), developed

in the usual manner. The flask is exposed to air after the third pass to check for residues of insoluble dye in the vat.

### **5.6. Dyeing of nanotubes**

At first, nanotubes dyeings were carried out at 50 °C. A sealed 1-dram vial with 30 mg of carbon nanotubes was purged with N<sub>2</sub> and placed into the water bath. Next, 2 ml of “leuco”, formed in the standard dyeing vat as above, was transferred via syringe into the vial containing nanotubes via syringe. After 15 minutes of dyeing, the tubes were suction filtered and in 30 minutes washed with 1% acetic acid solution. After the nanotubes were dried, half of the sample was placed in boiling water for 10 min for thermochromic studies. Later nanotube dyeings with the multi-walled nanotubes were performed at reflux in an apparatus consisting of a 15-mL 3-neck round-bottom flask under N<sub>2</sub>, fitted with a reflux condenser and magnetic stirring bar.

### **5.7. TEM analysis**

A suspension of MBI-dyed carbon nanotubes (1 mg) in acetonitrile (1 mL) was diluted by a factor of 37 and was sonicated for 30 s. A 8- $\mu$ L drop of the diluted suspension was placed on a 300-mesh carbon-coated copper grid (TED Pella Inc., Redding, California, USA) and was allowed to dry for 1 min. The excess liquid was removed using filter paper. Energy Dispersive X-Ray Spectroscopy analysis (performed by EDAX) confirmed the presence of bromine atoms, most likely within the darker areas of the image. These areas represent MBI molecular aggregates. A control sample prepared in the same way in the absence of MBI did not show these darker areas in the image. Since a carbon-coated grid was used and carbon nanotubes were present in the mixture, the Netcounts method (sample area minus control area) [Samson et al.,

2011] was not used. As a result, the X-ray scattered lines from the copper grid showed up in the background of the spectrum. In order to avoid solvent effects, later samples of multiwalled nanotubes were prepared by loading a dry sample into the grid directly with use of a pipette bulb.

## **Acknowledgments**

When I entered Baruch College as a freshman I had no idea what a wild ride it would be, yet I could not be more grateful for the opportunities this small and affordable school had to offer. Having switched to the Biology major on my second year was the best decision I've made so far. And now, upon completing the last semester at this college, I would like to express my gratefulness to all the people who have been helping me to unveil my true passion and realize my dream of becoming a doctor.

The Honors thesis has become a culminating point of my journey at Baruch College. During this project I've not simply put the skills I acquired at the school to the test but I was also rewarded with the discoveries revealed in the laboratory made possible as a result of dedicated, tenacious and passionate work.

I would like to thank my amazing mentor - professor of organic chemistry Dr. Keith Ramig, who has kindly introduced me to the project involving the ancient dyes and patiently led me through the peculiarities of the laboratory techniques which were essential in carrying out the studies. Moreover, Dr. Ramig has helped me grow as a scientist by encouraging us to critically analyze each step of our project and think outside the box while solving the problems.

I would also like to express my endless gratitude to the professor of general chemistry, Dr. David Szalda who has introduced me to the world of chemistry and helped me understand such difficult concepts like Molecular Orbital Theory; and Dr. Edyta Greer, who made me fall in love with organic chemistry and pursue a research in that particular field.

While my undergraduate major states "Biology"- I most definitely think of myself as a chemist with the keen interest in interactions of the positive and negative charges of organic compounds.

Looking back at my career path of three years ago, I couldn't even imagine myself getting into a medical school in fall 2013. My life has turned around drastically as I took my first biology class with the amazing professor Dr. Emil Gernert whose contagious passion for science inspired many students of Baruch College to change their career paths. I am endlessly grateful for his insightful advice and support through the difficult years of studying science.

In addition, I would like to express my gratitude to all the professors and the whole staff of Baruch's Natural Science department who are always there to help students like myself to realize and follow their dreams.

Last but not the least, I'd like to admiringly mention those people who have played an integral role in my research: I greatly appreciate the help of my dear friend and laboratory partner Allen Ko, who has often assisted me during the project; Dr. Jacopo Samson from Hunter College who significantly added to my investigation of the organic dyes with TEM imaging; Federica Pozzi from City College and Hiroko Ajiki from Hunter College for providing reflectance spectra, Dr. Sasan Karimi from Queensborough Community College for supplying us with DBI and Rachel Kravetz from Baruch's writing center for helping me with editing and grammar of this paper.

In conclusion, I would like to thank all of my friends for their support and particularly acknowledge my best friend - Olesya Medvedeva - who has been encouraging me for all these years to always move forward and never give up.

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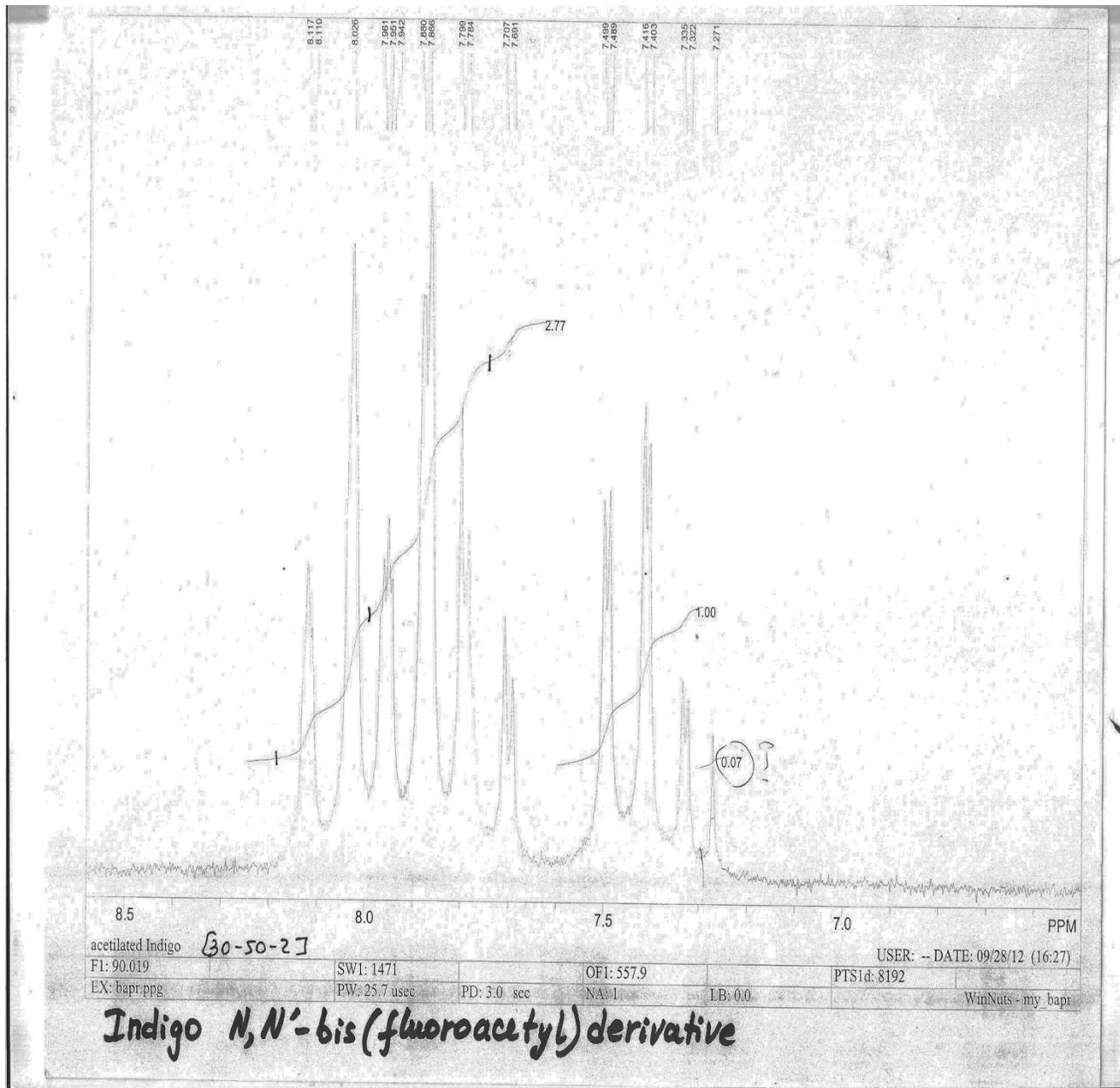
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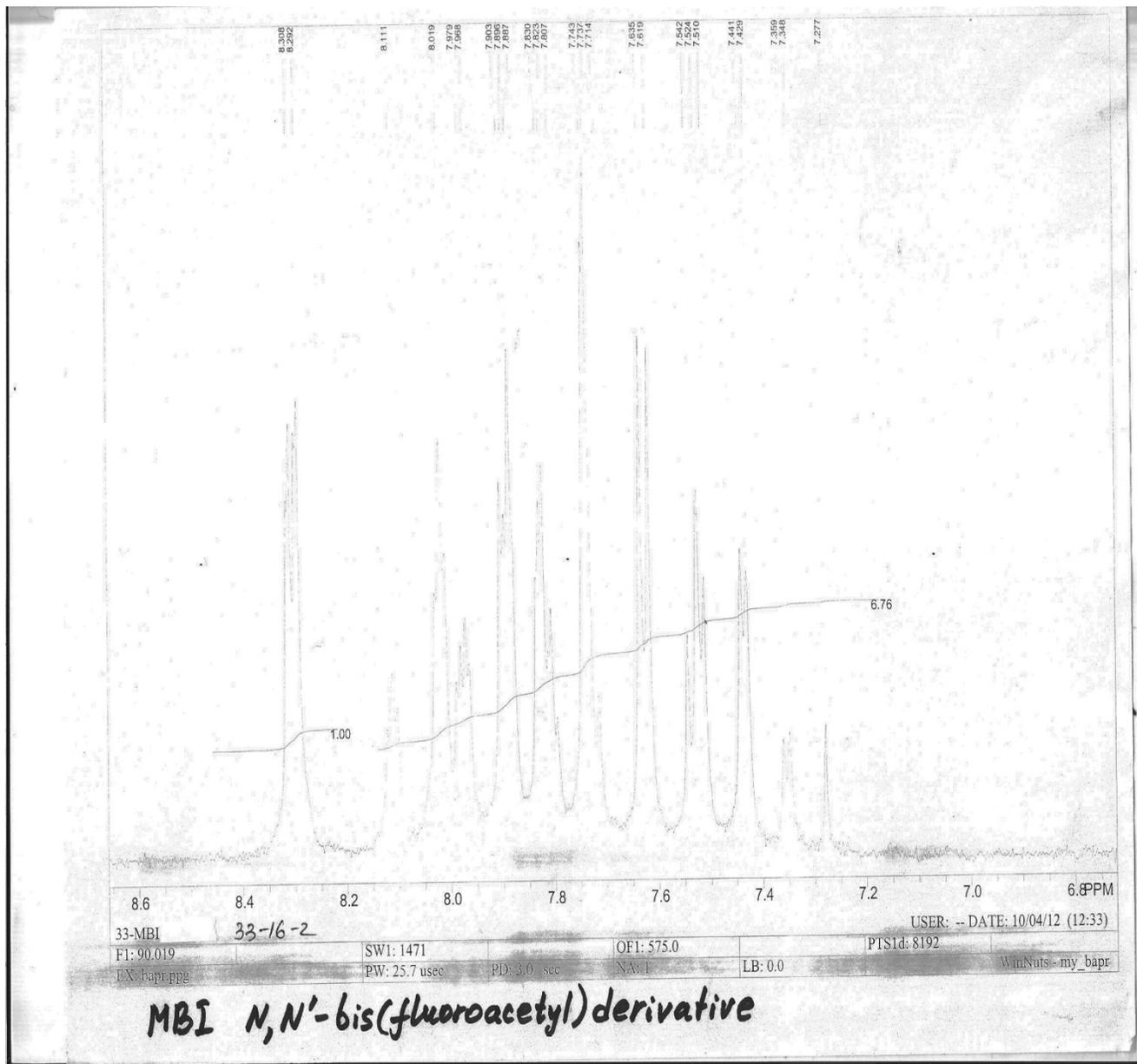
# Appendix A

## <sup>1</sup>H NMR spectra

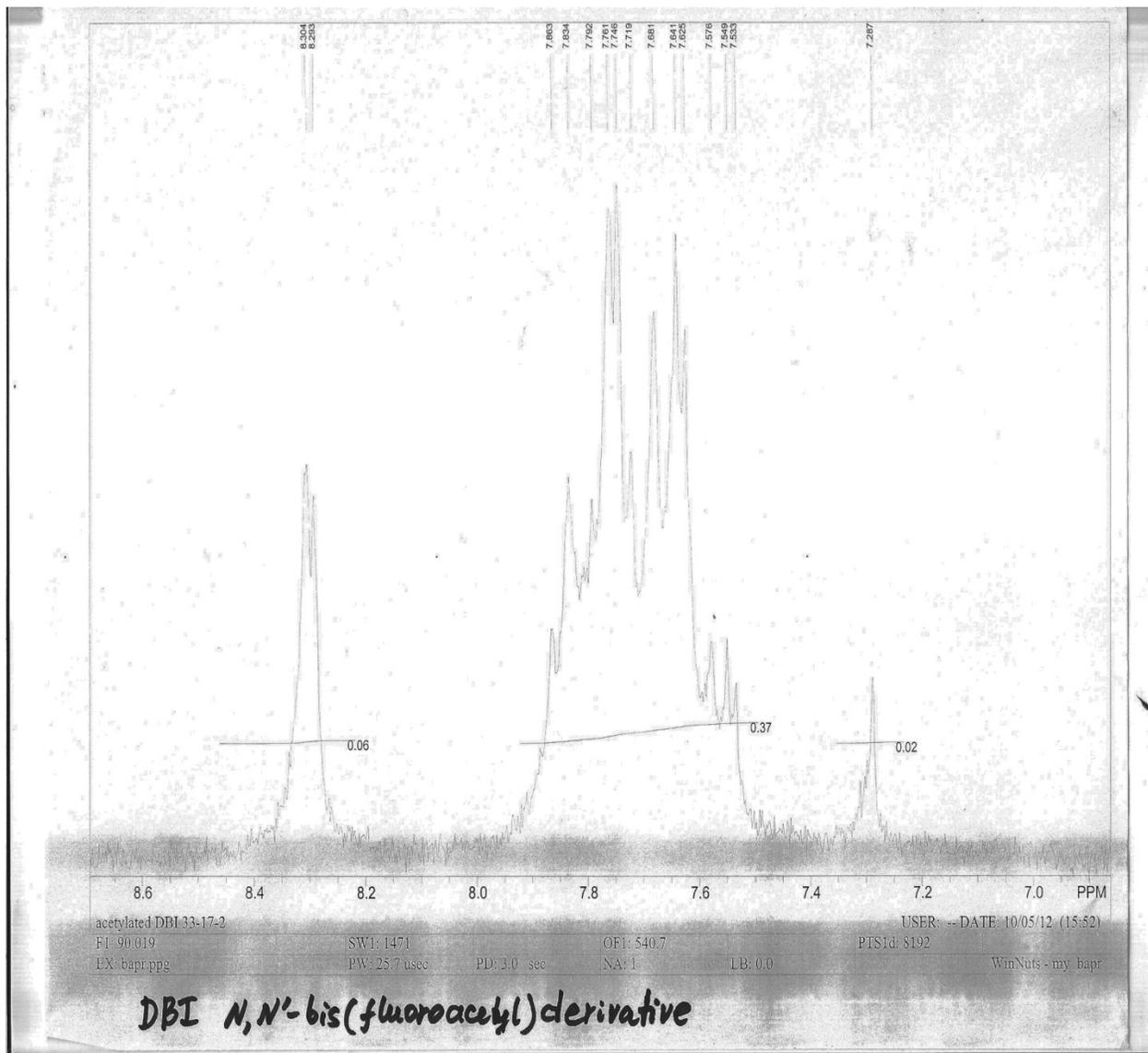
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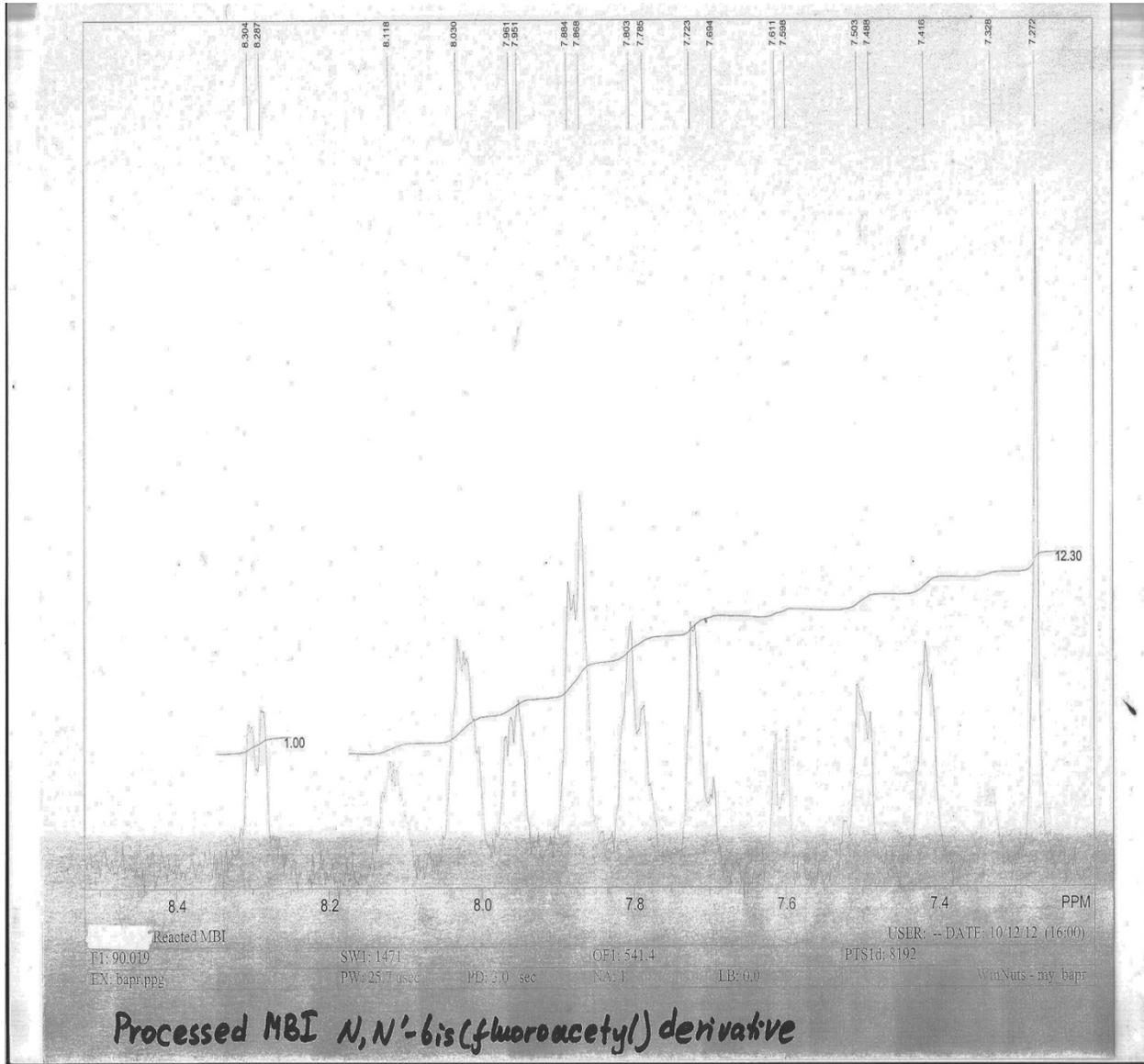
MBI, bis N, N'-trifluoroacetyl derivative



DBI, bis N, N'-trifluoroacetyl derivative



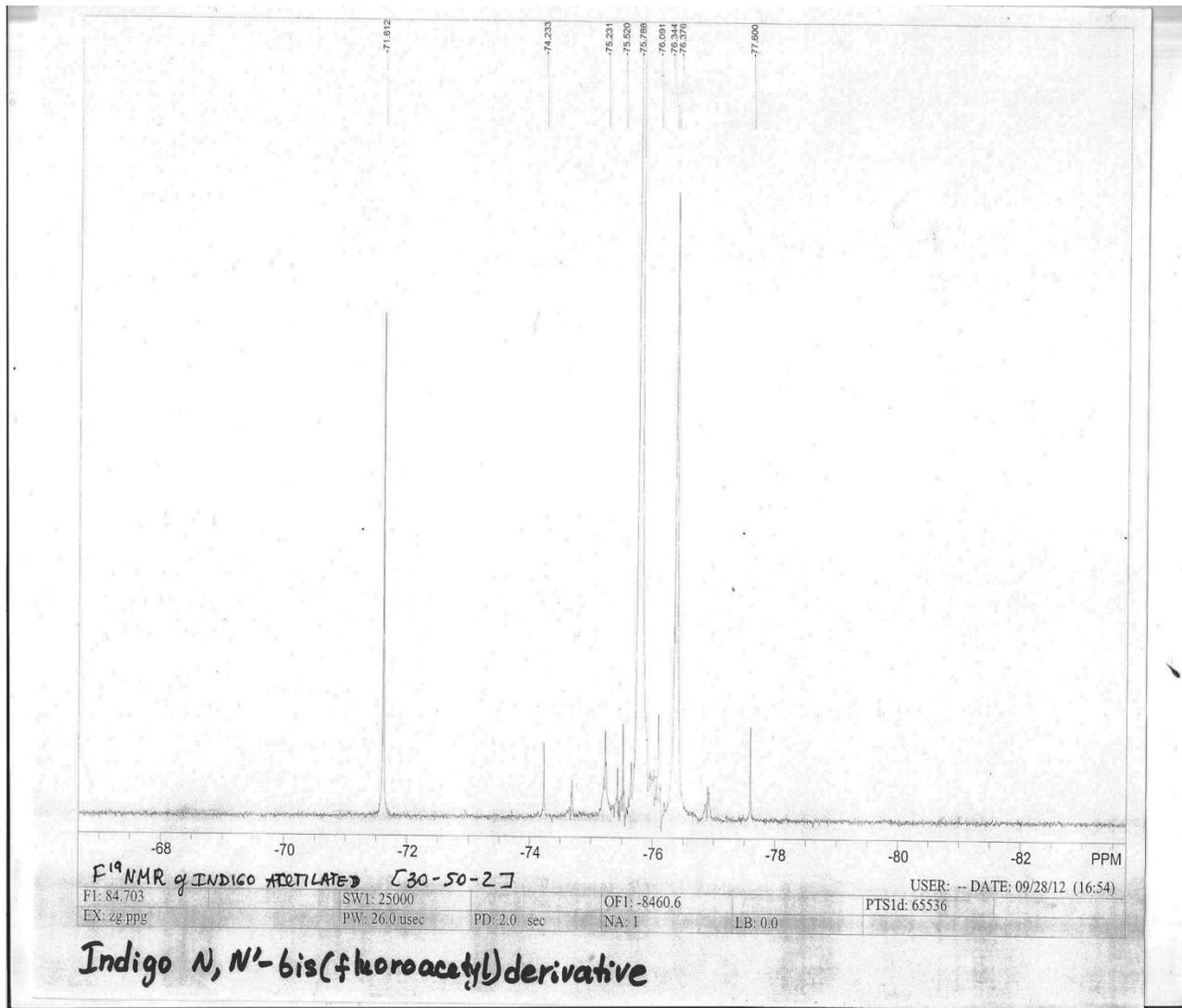
MBI converted to "leuco" and oxidized back to solid



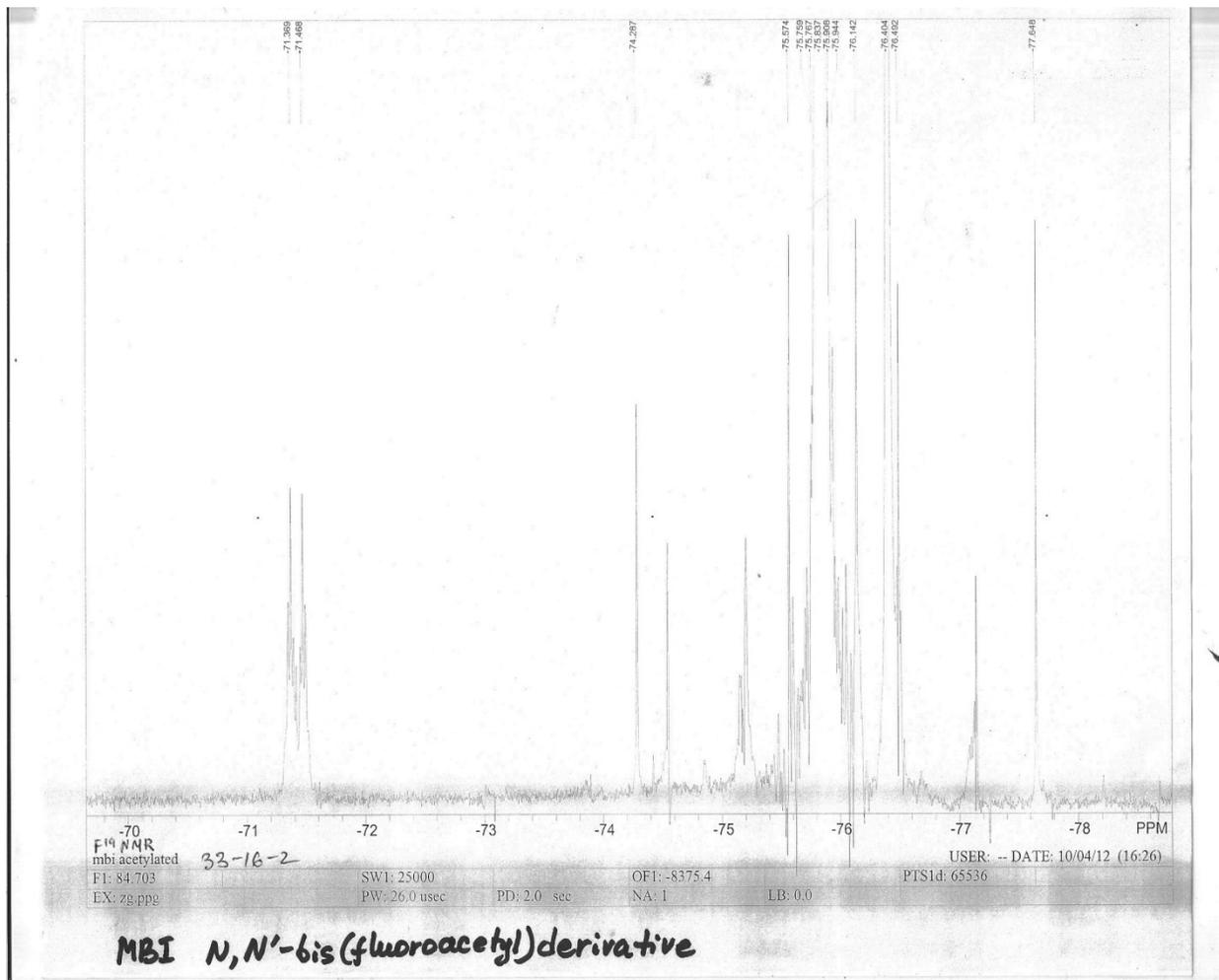
# Appendix B

## 19F NMR

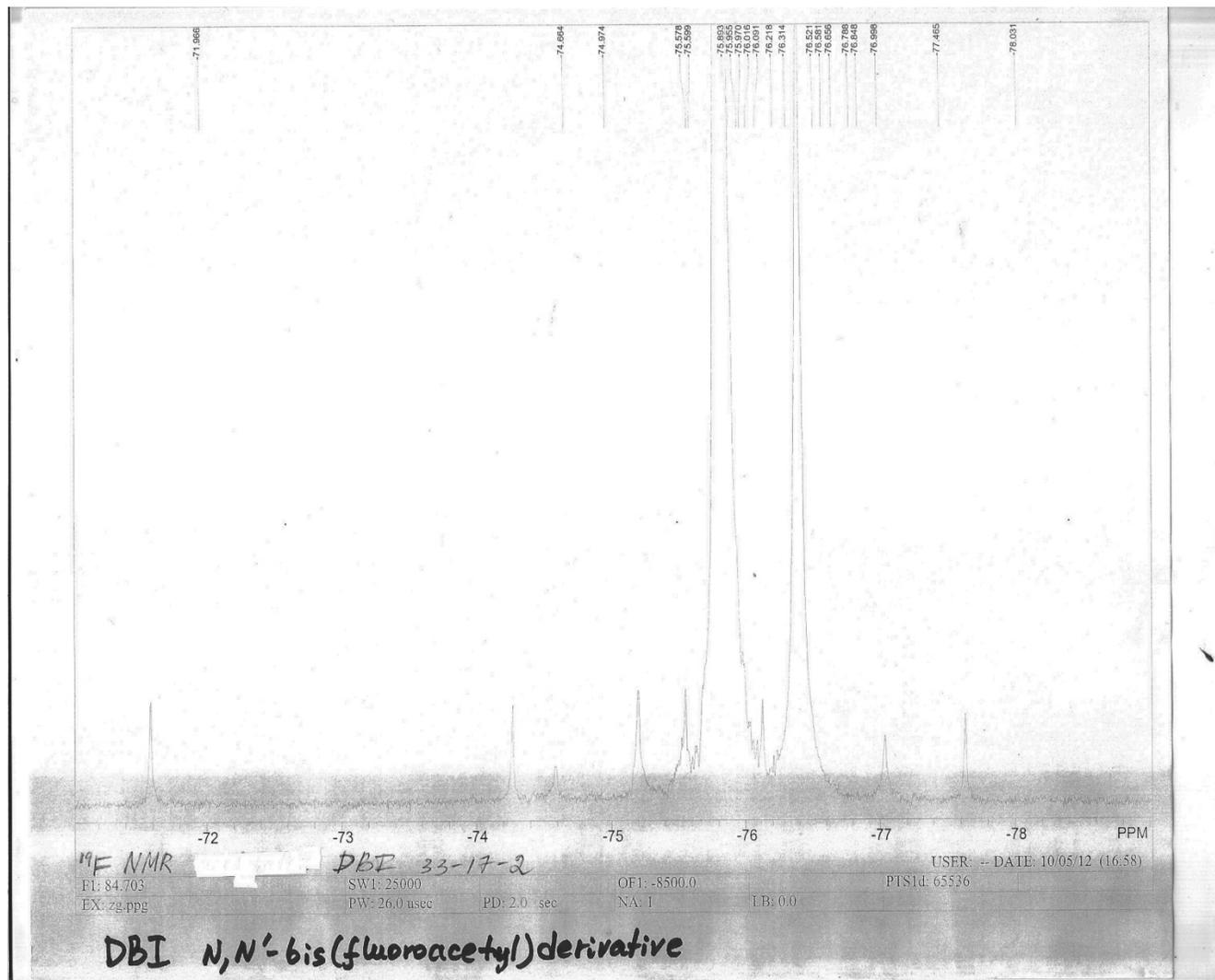
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MBI, bis N, N'-trifluoroacetyl derivative



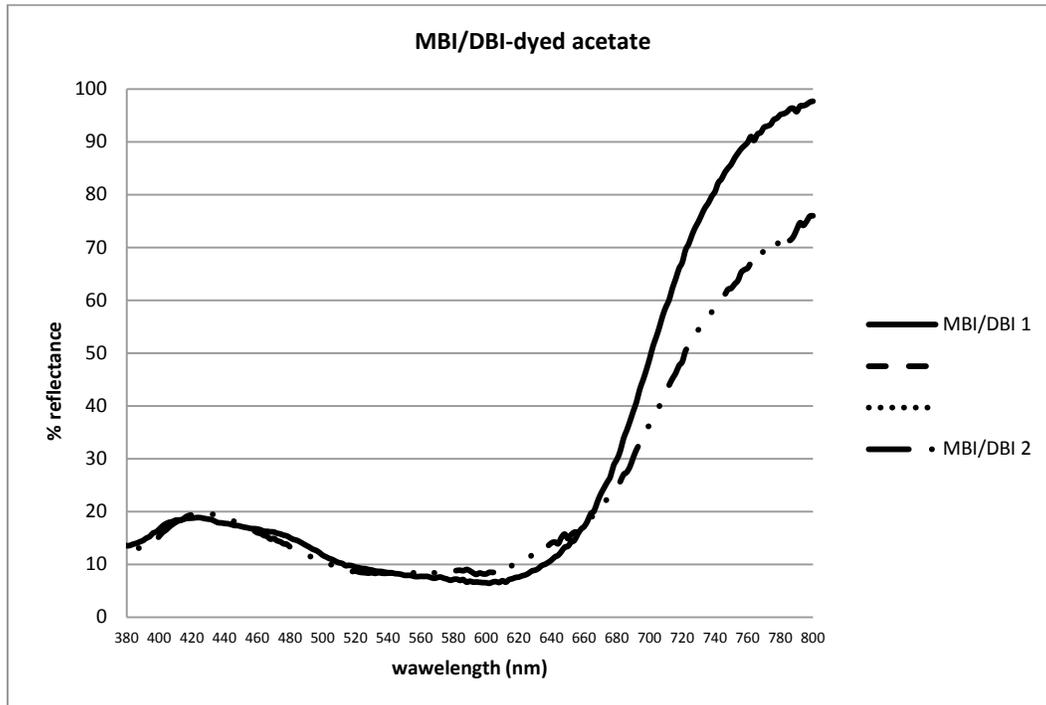
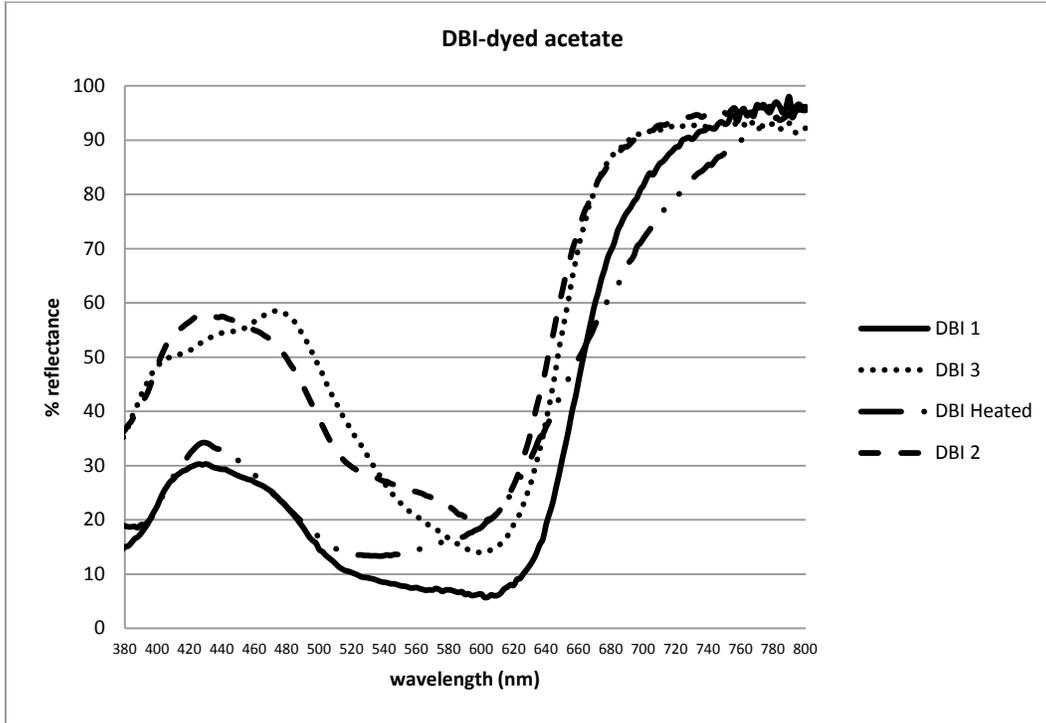
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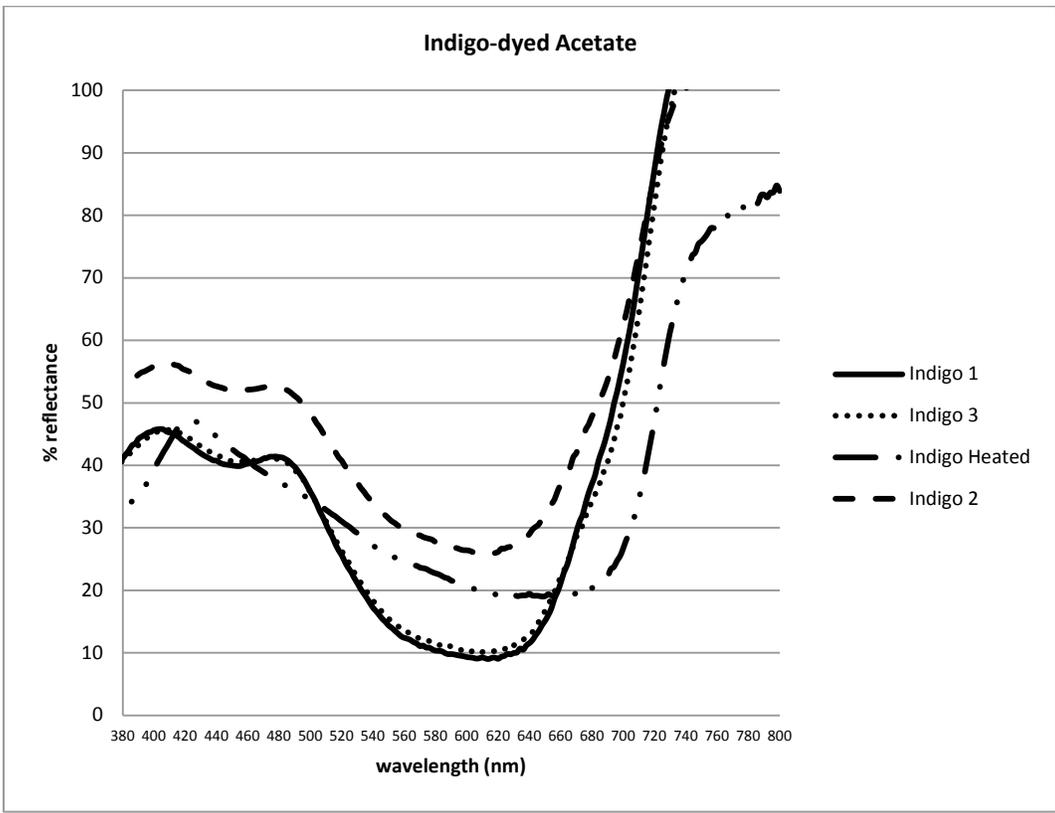
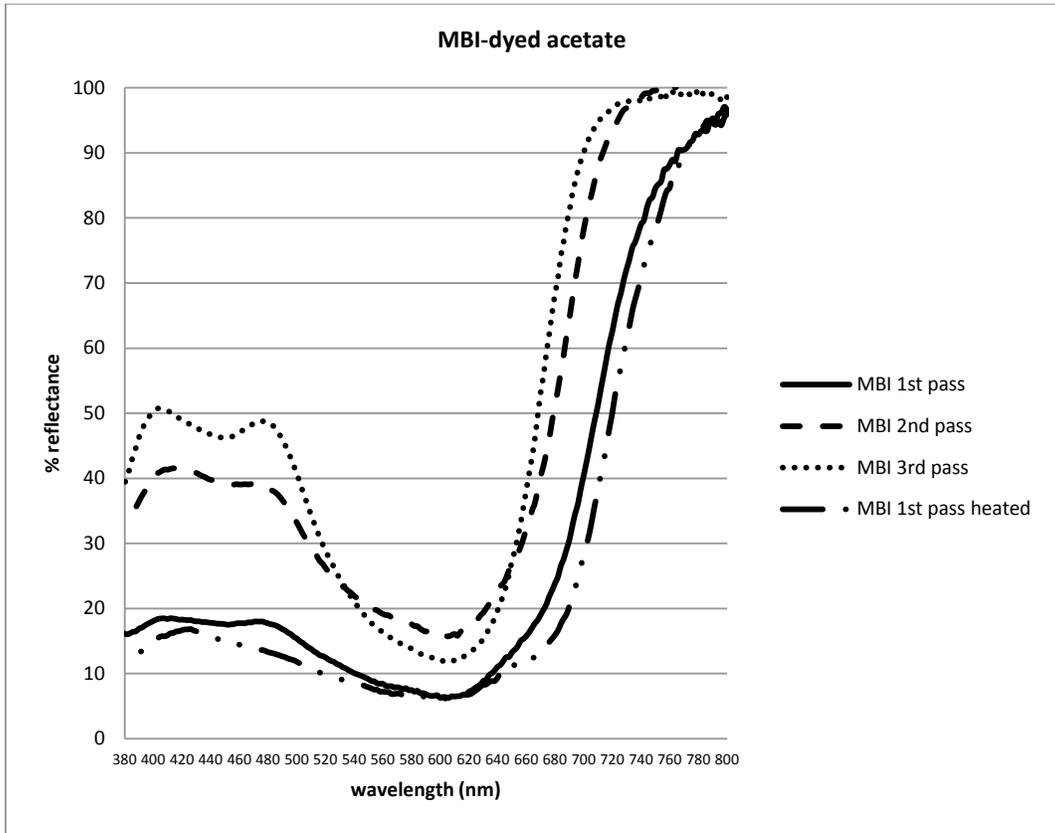


## Appendix C

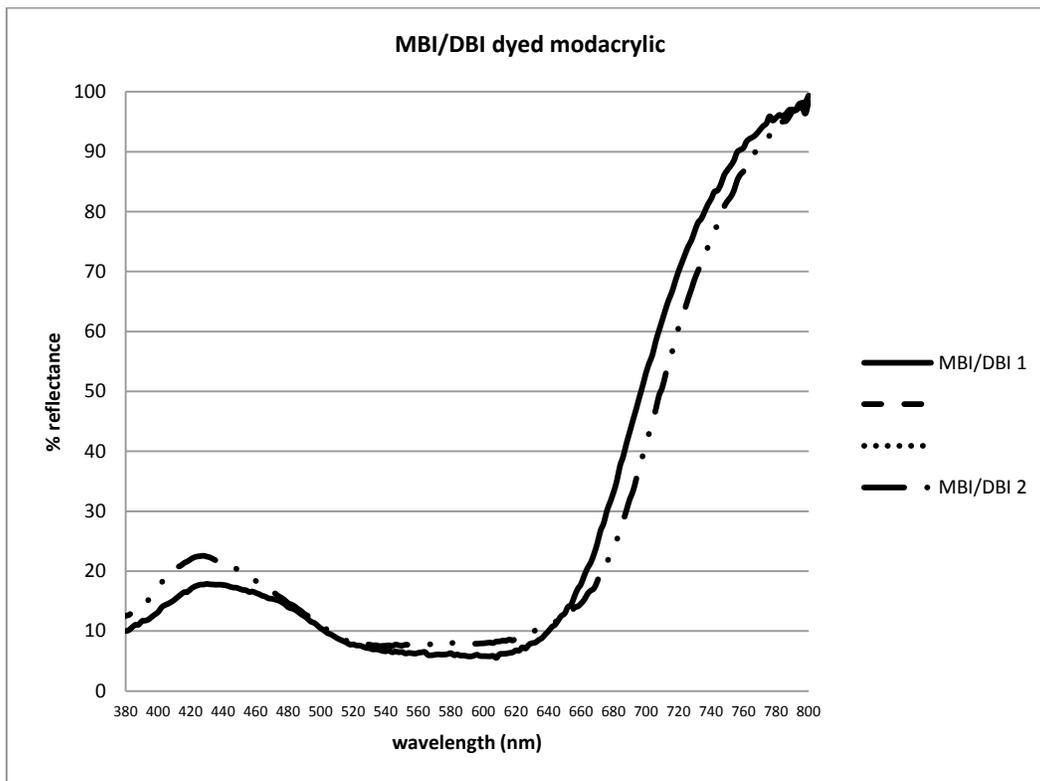
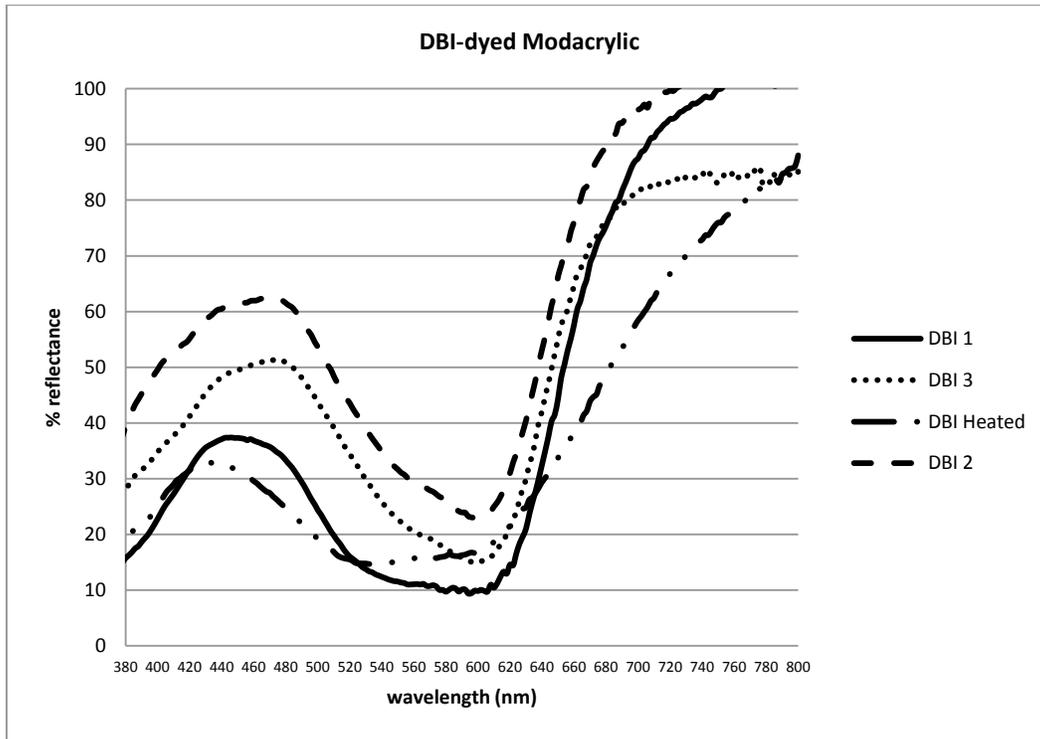
Note: number in the name of a series indicates pass (exp. DBI 1 – DBI-dyed fabric, first pass), except for MBI/DBI-dyed spectra, where MBI/DBI 1 indicates fabric before heating and MBI/DBI 2 indicated fabric after heating.

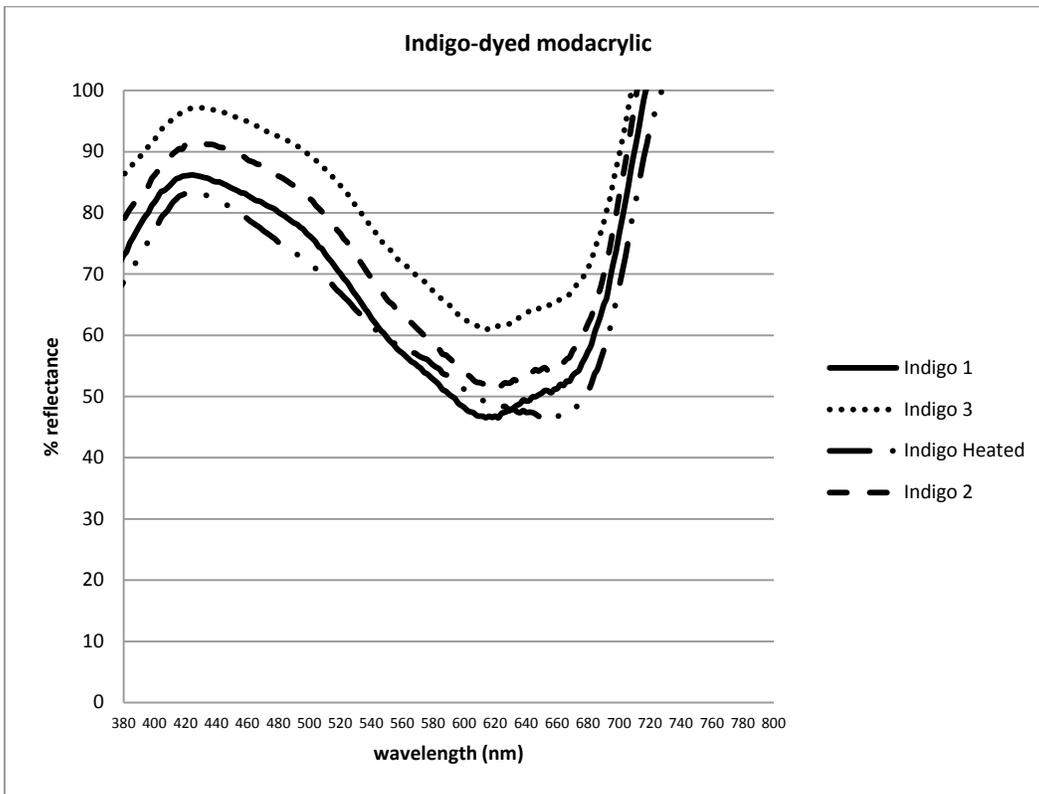
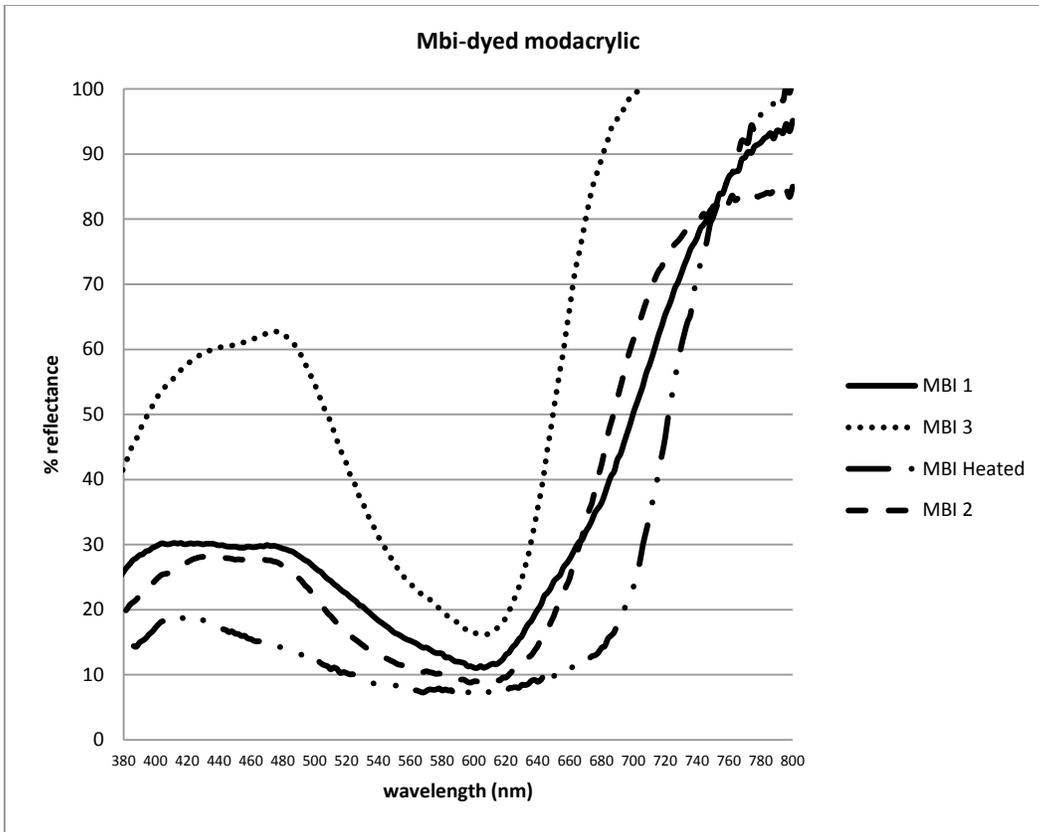
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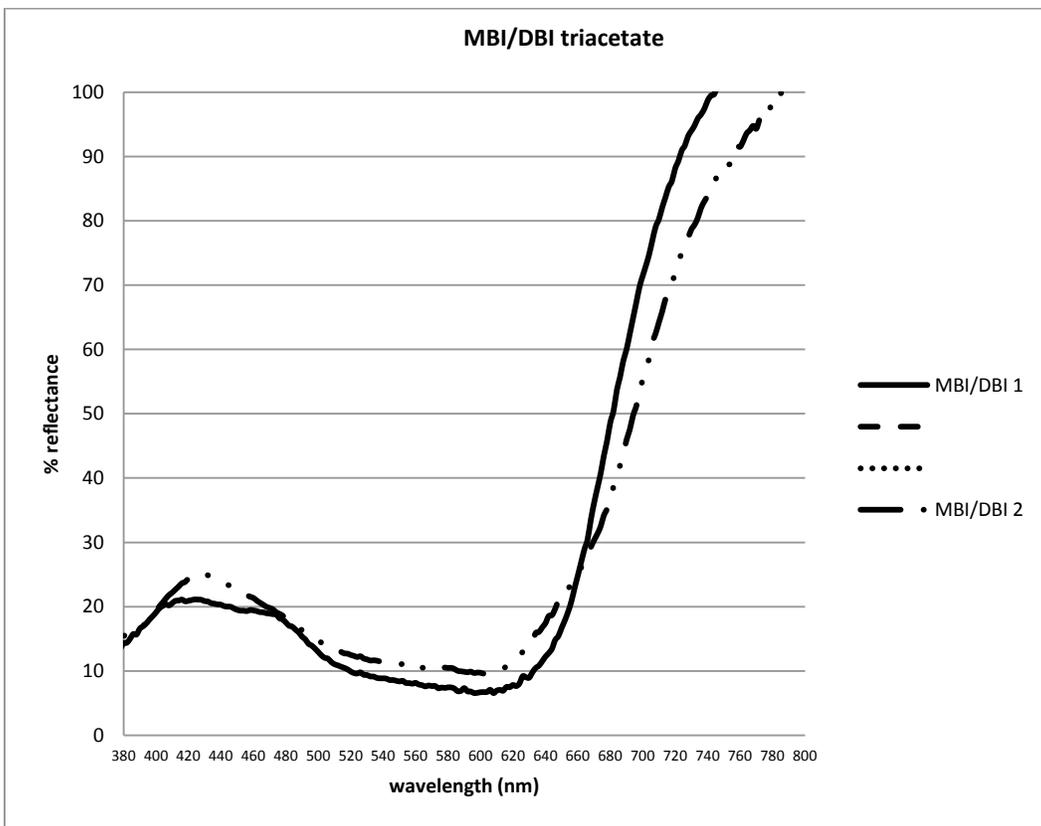
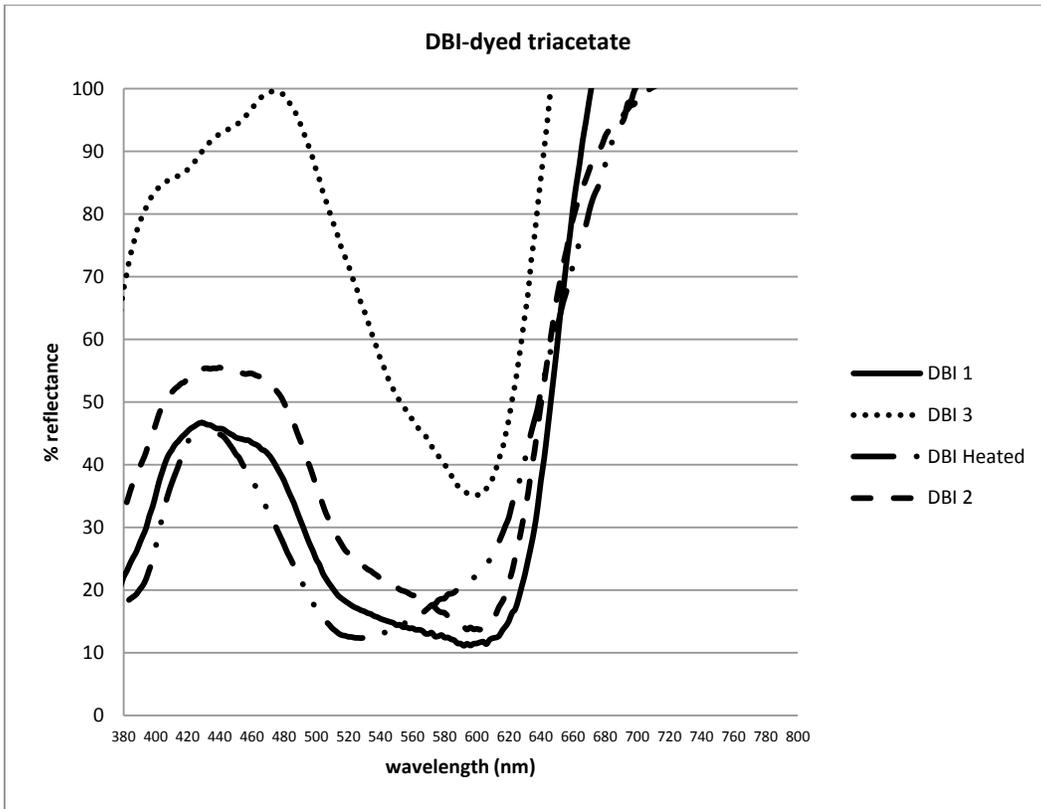


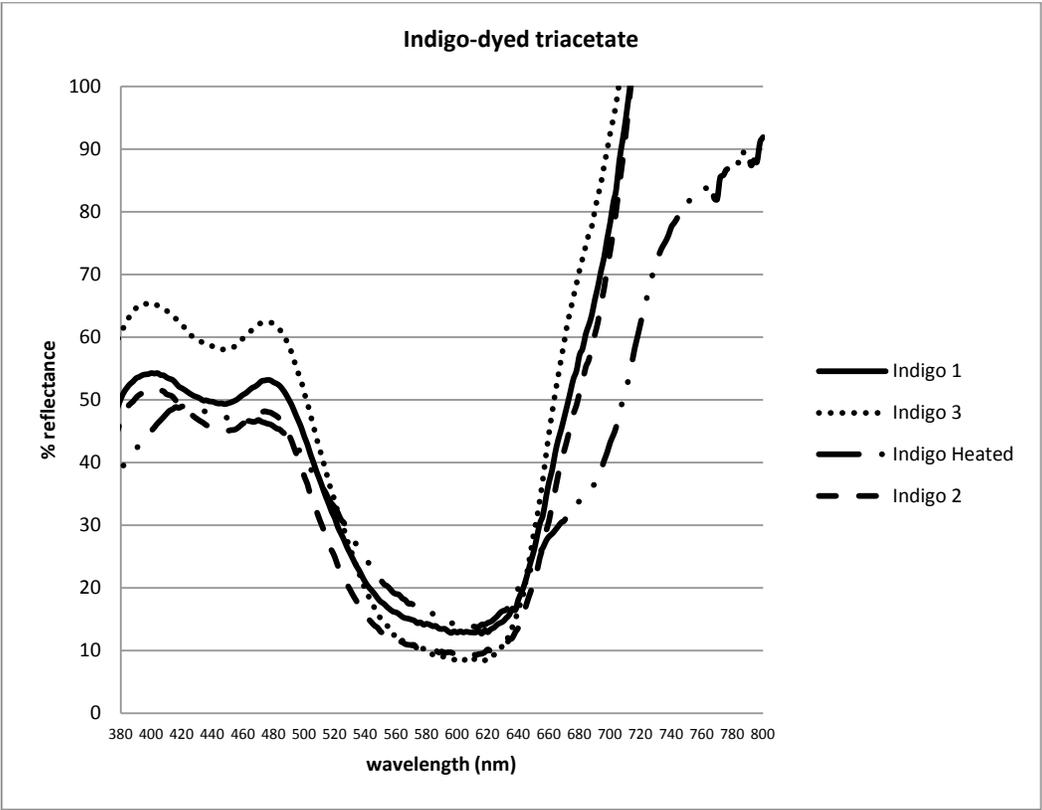
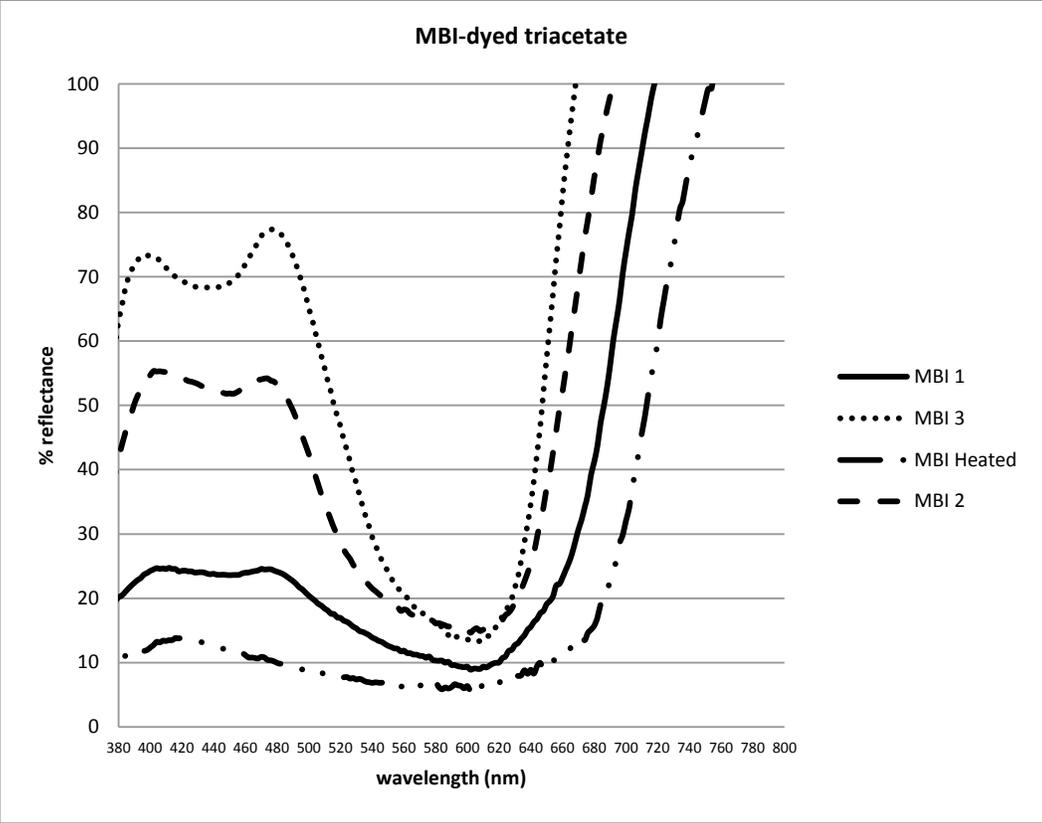
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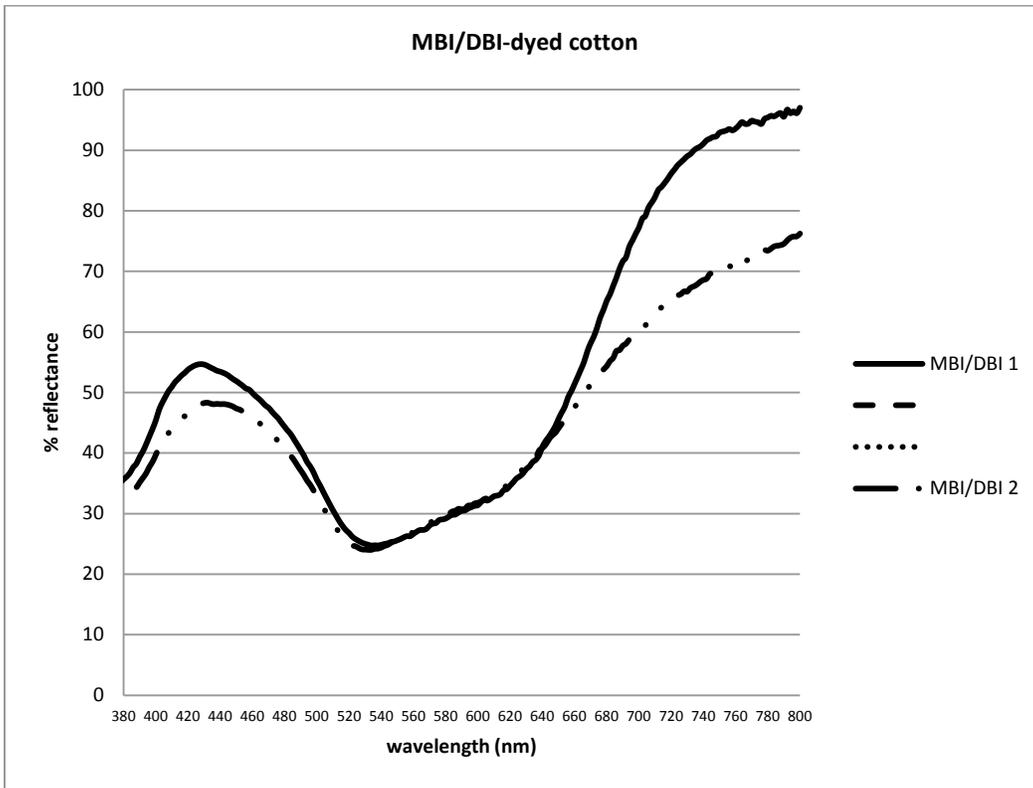
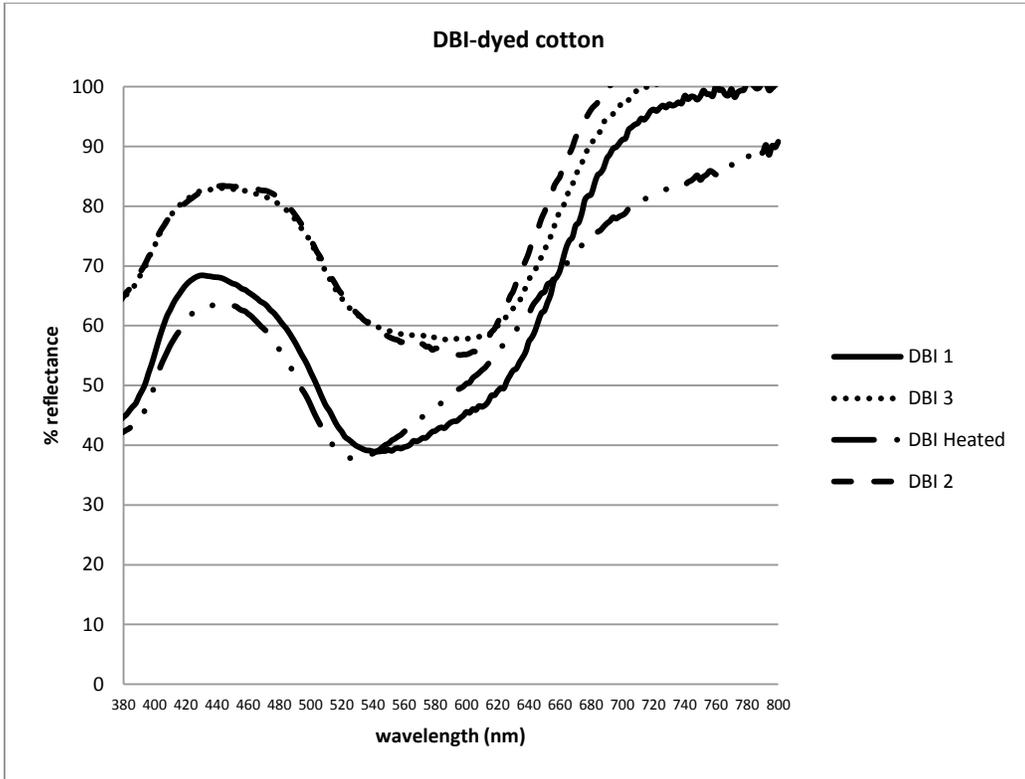


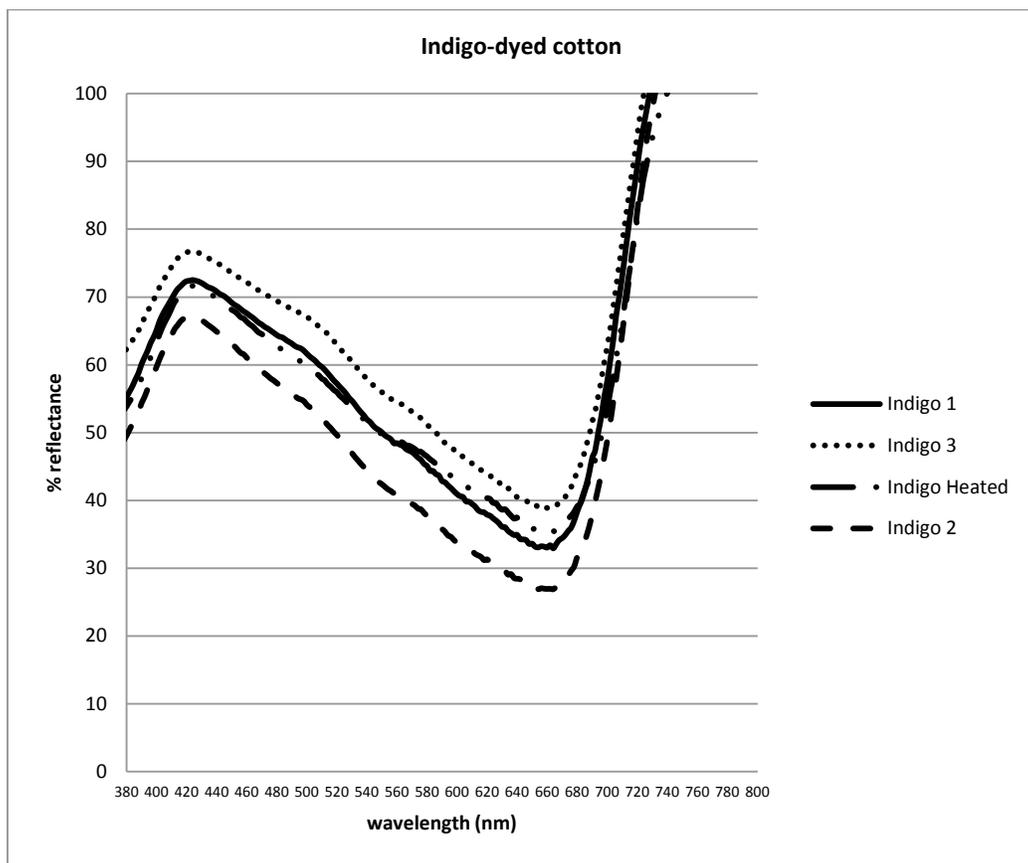
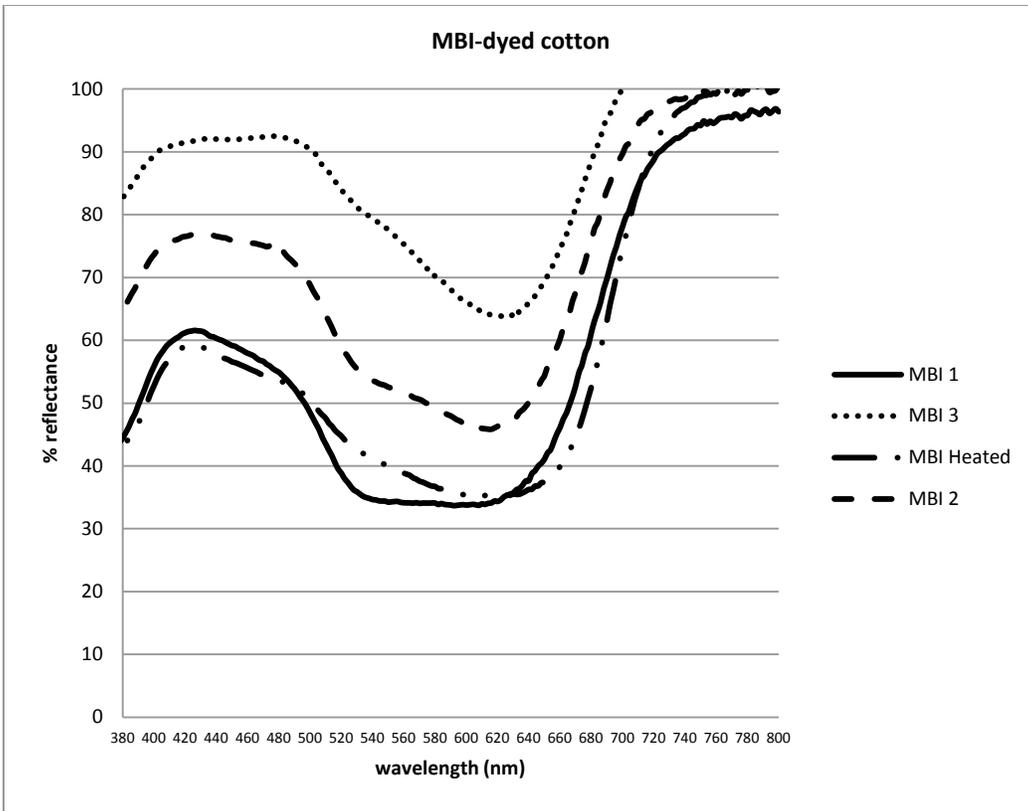
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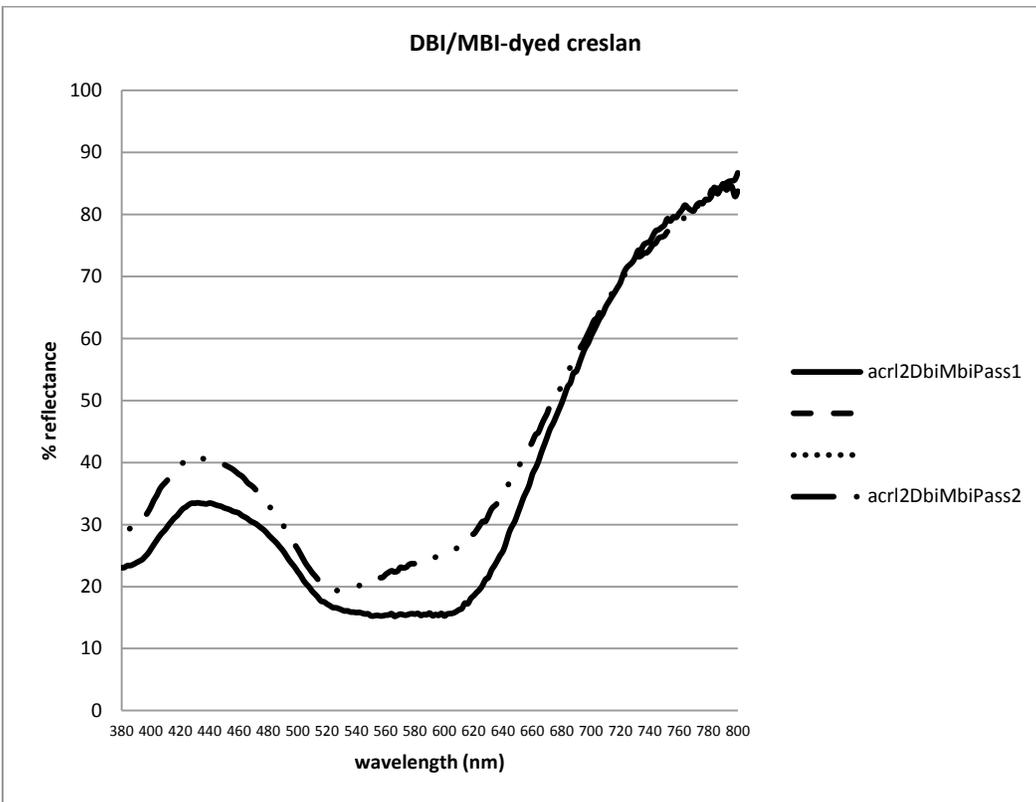
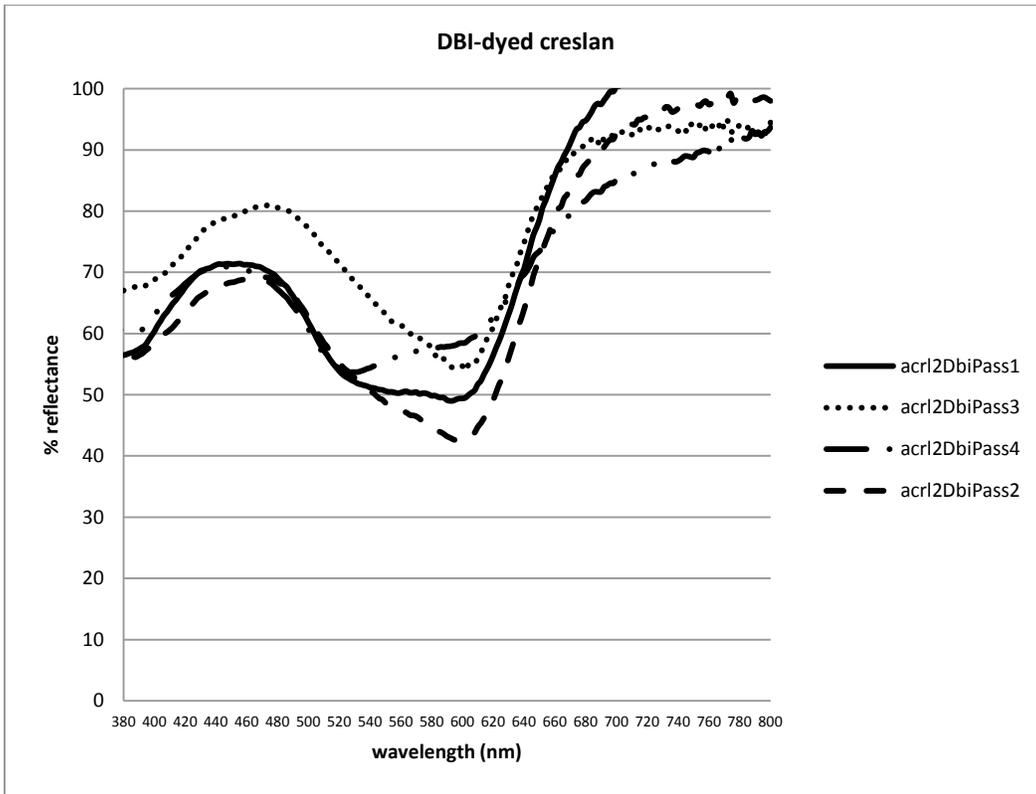


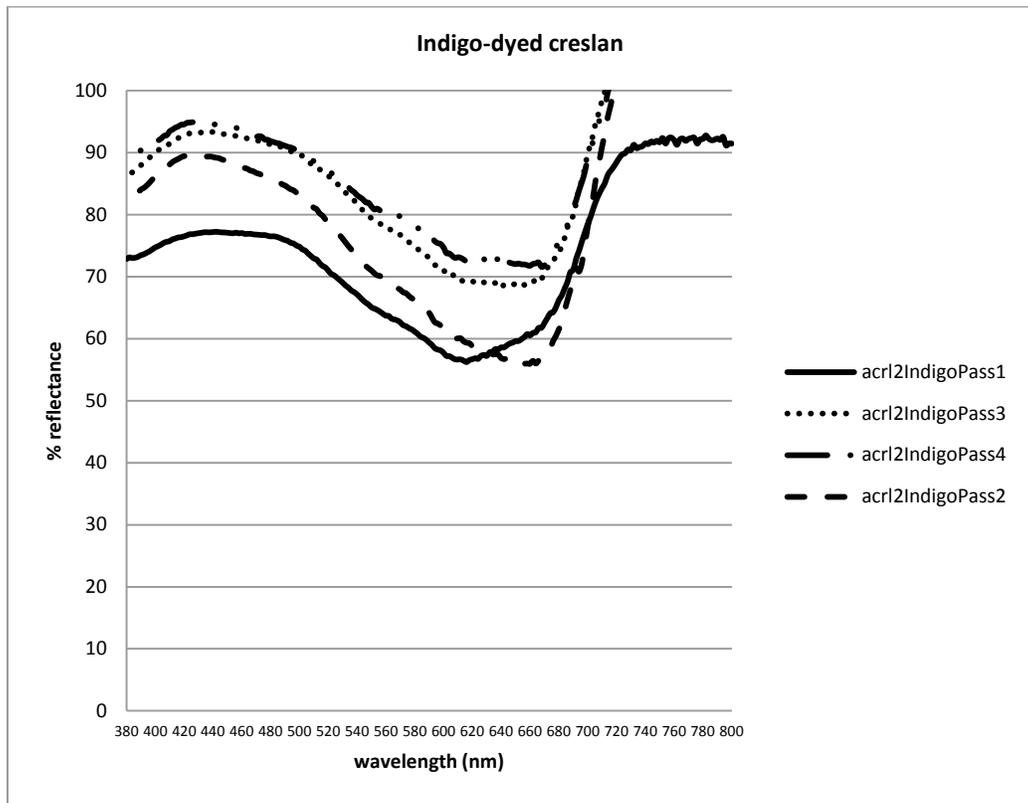
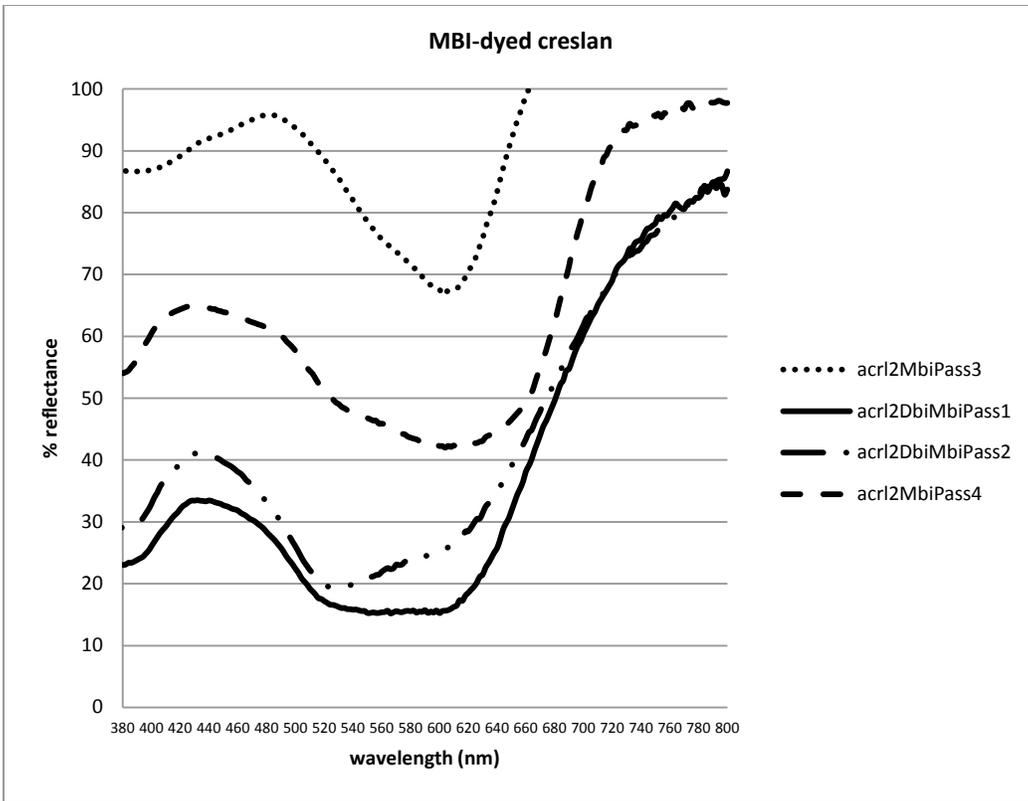
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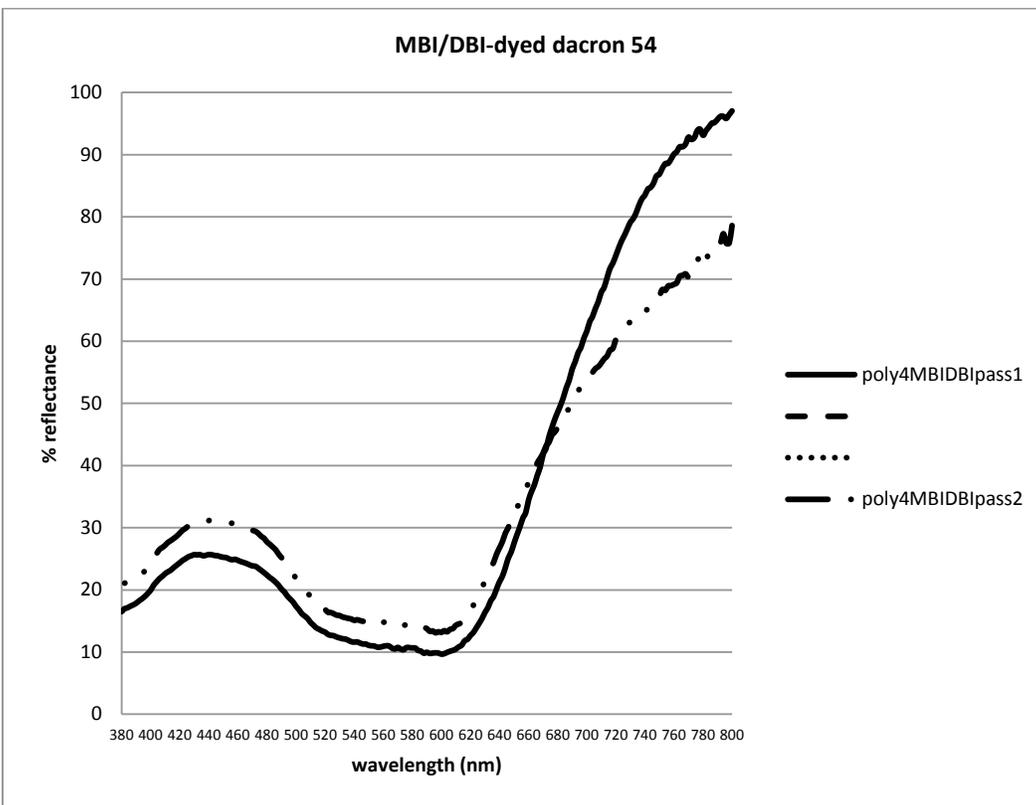
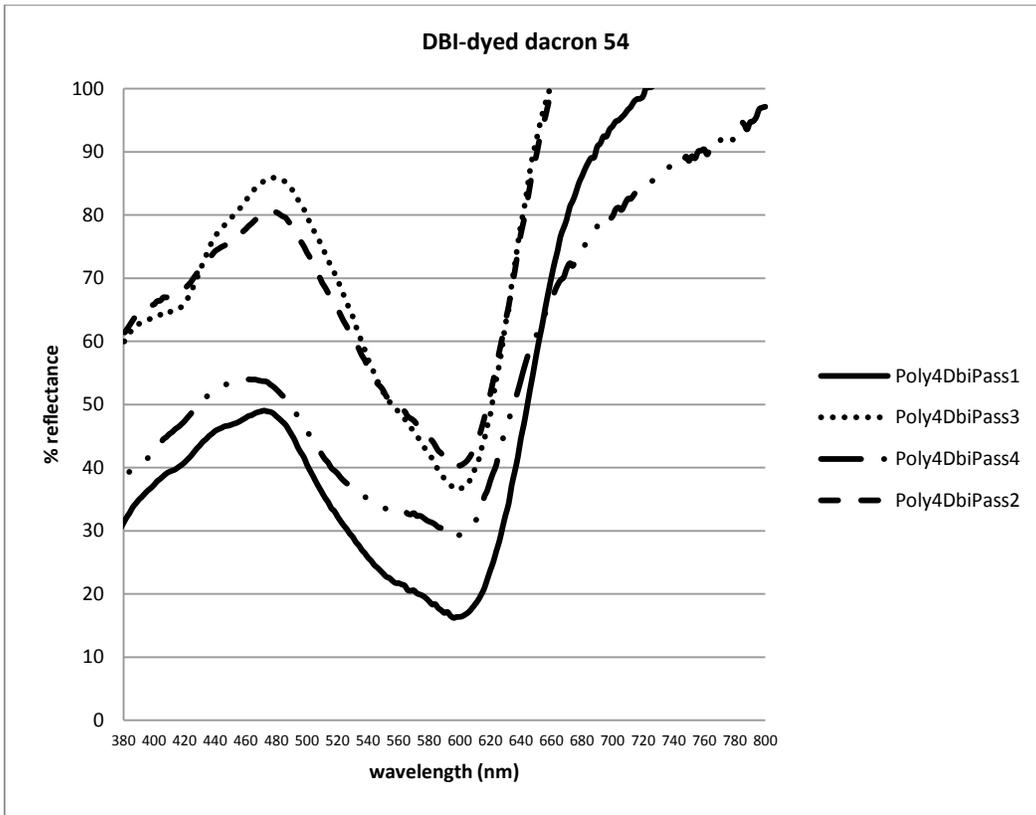


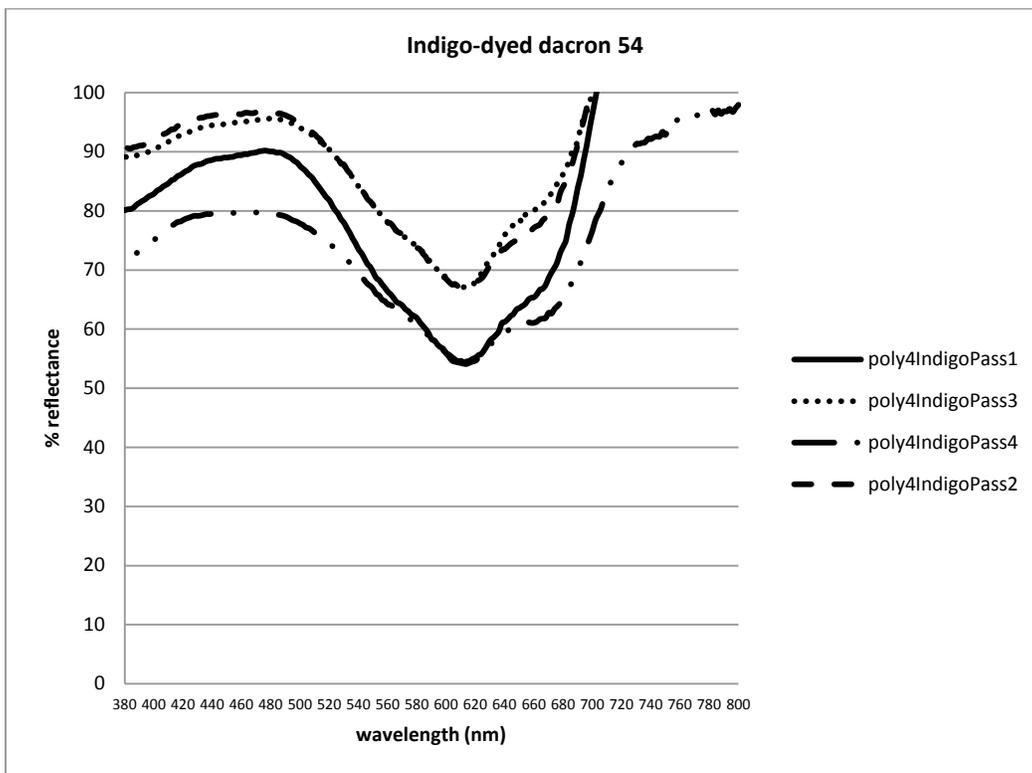
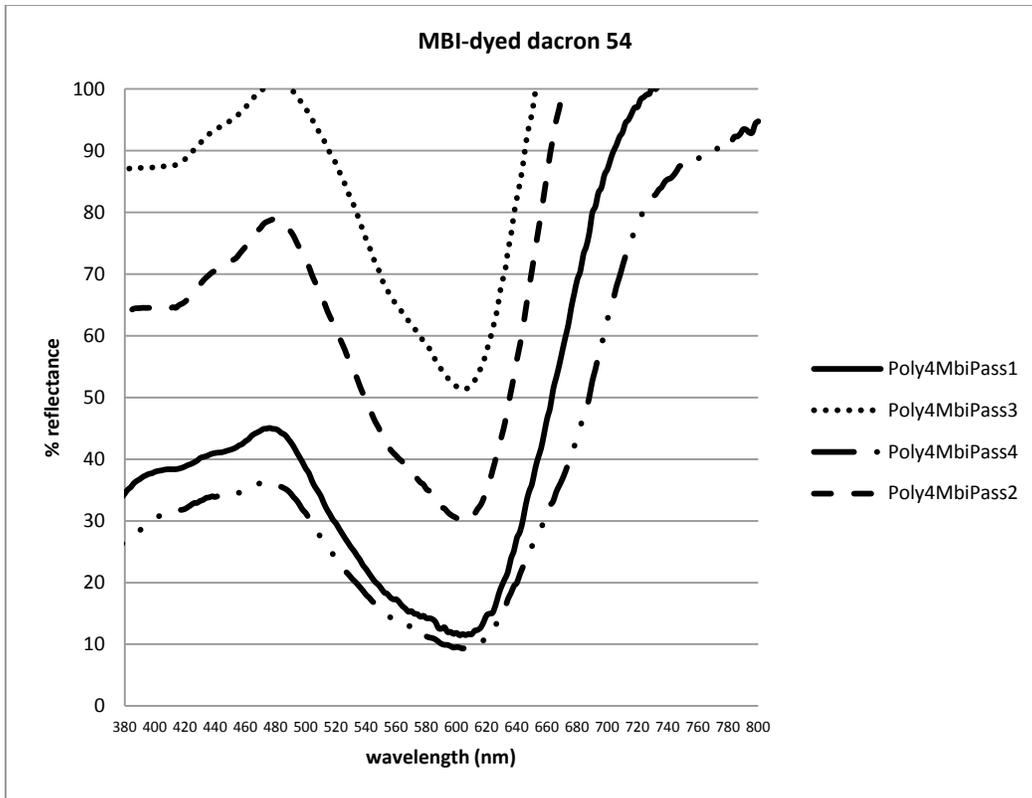
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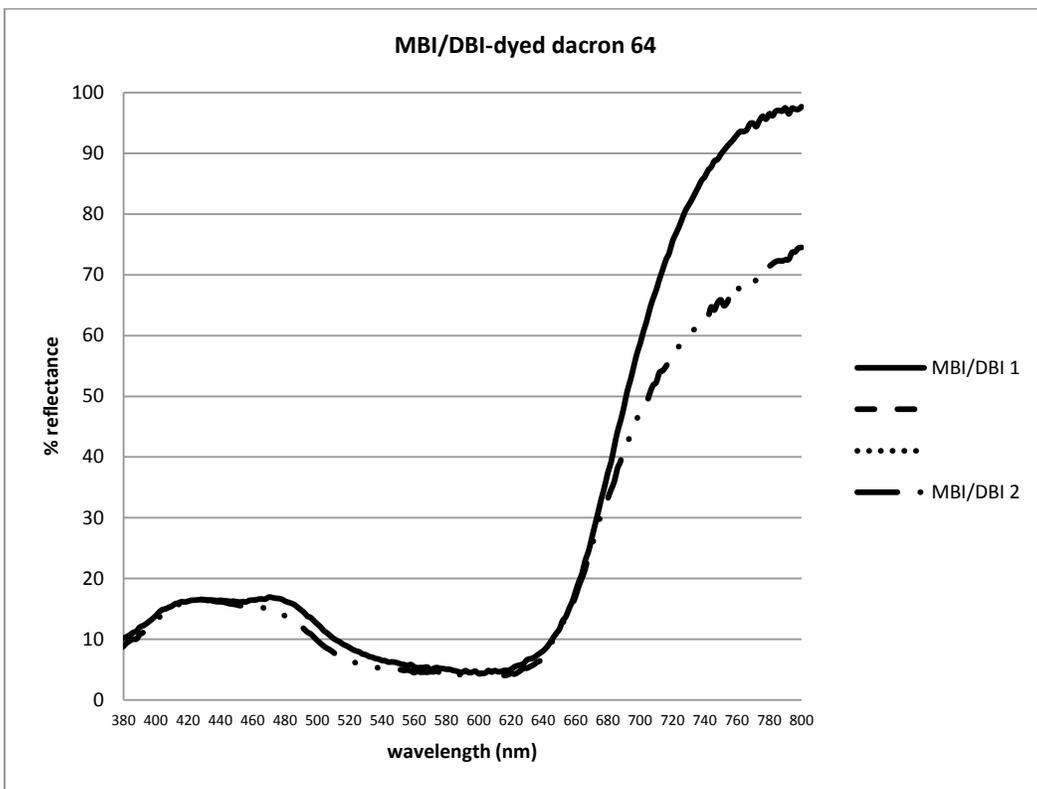
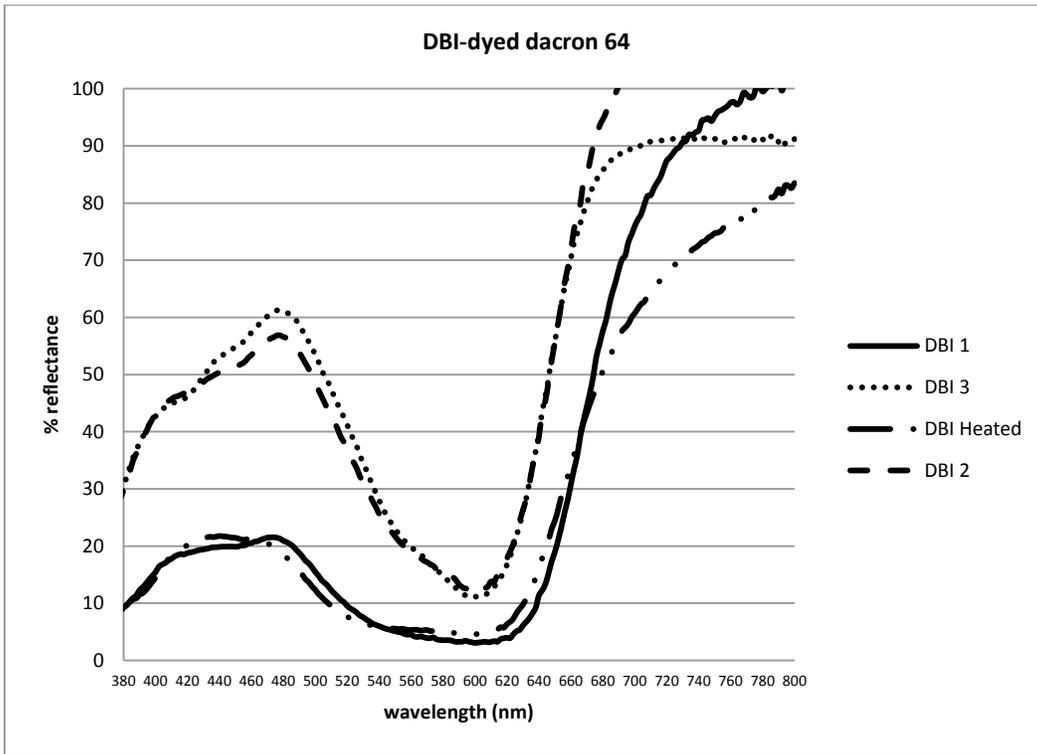


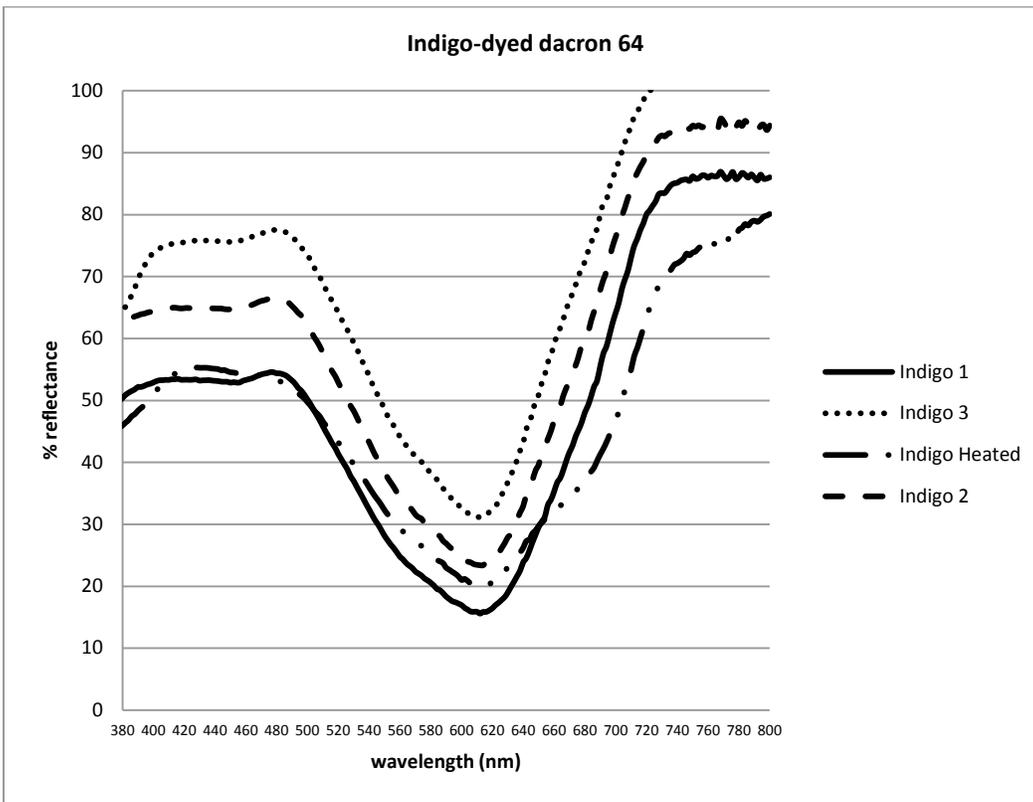
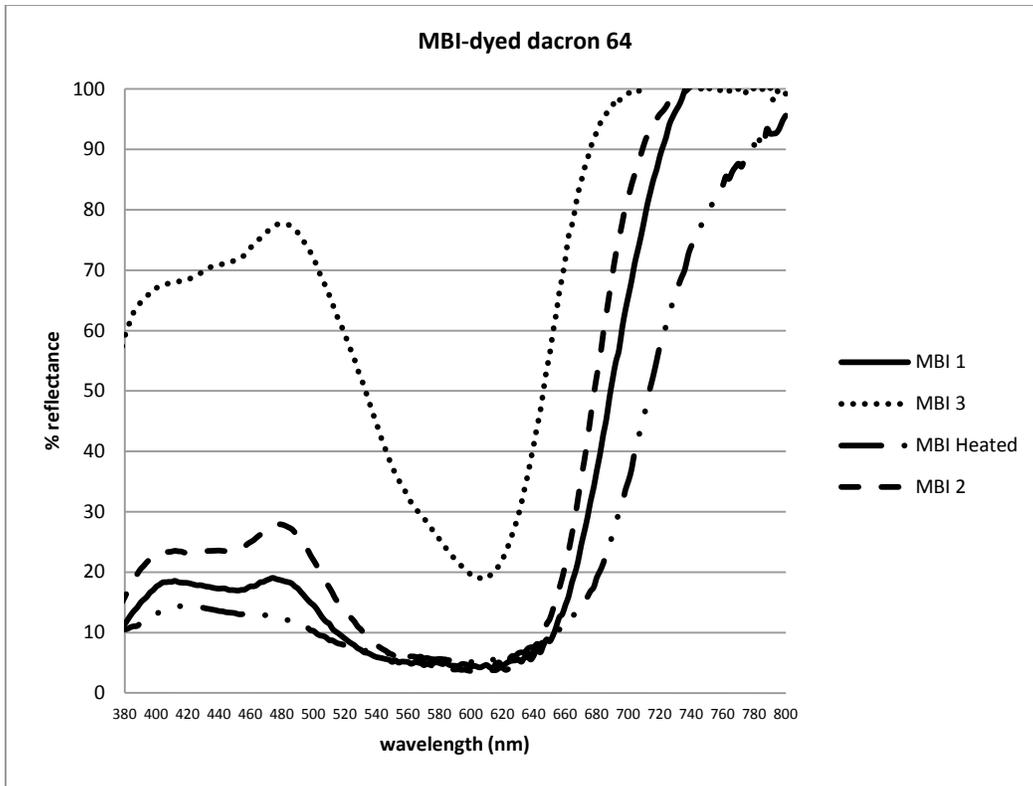
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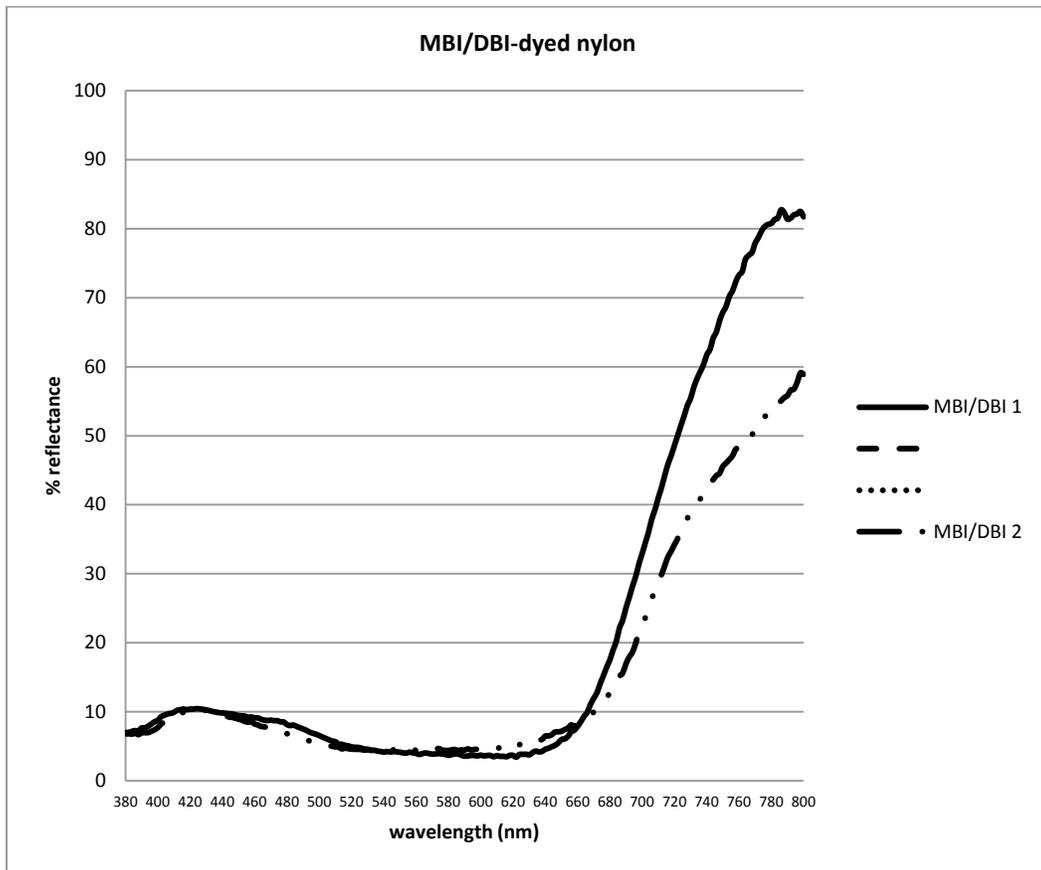
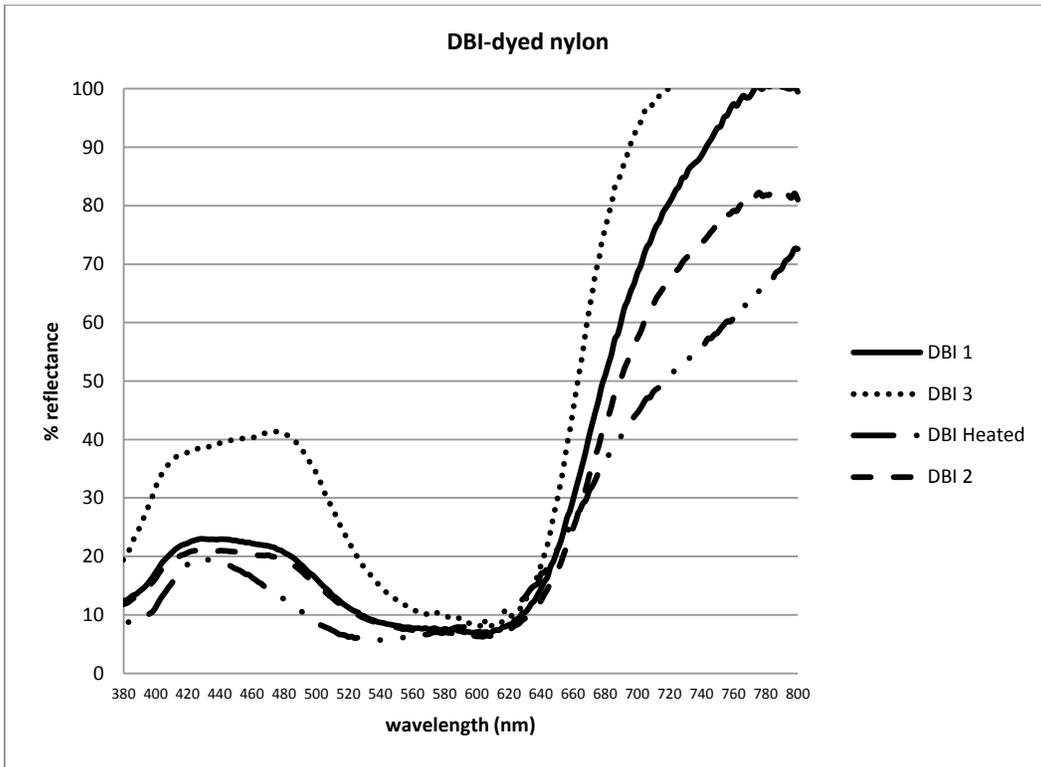


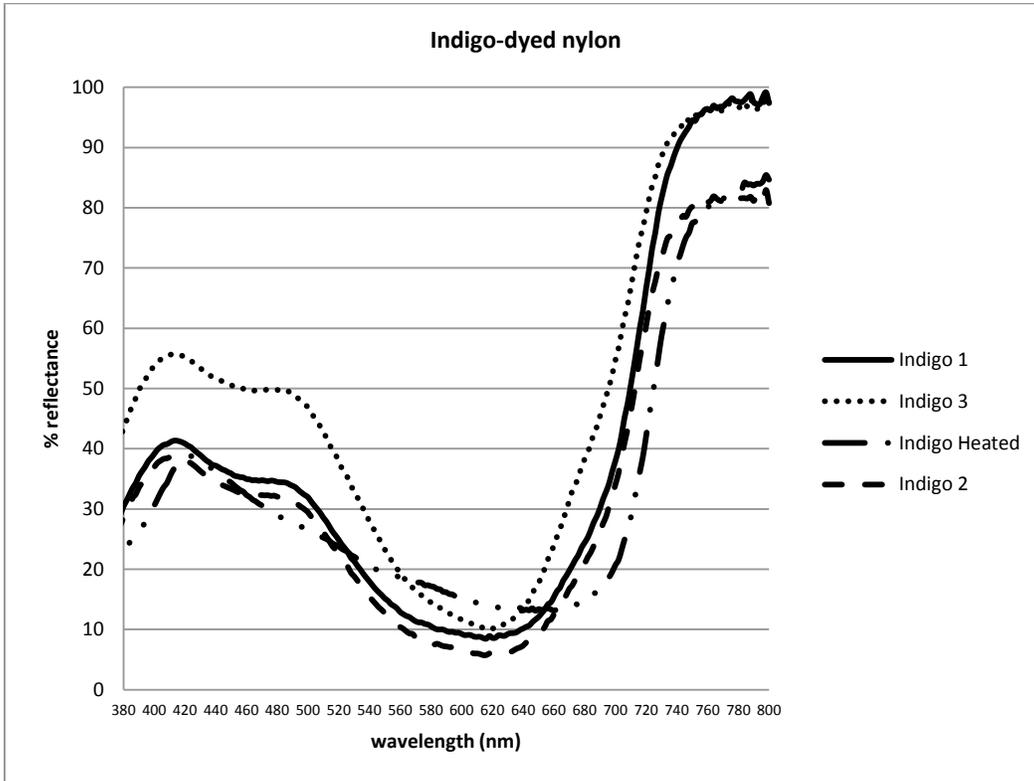
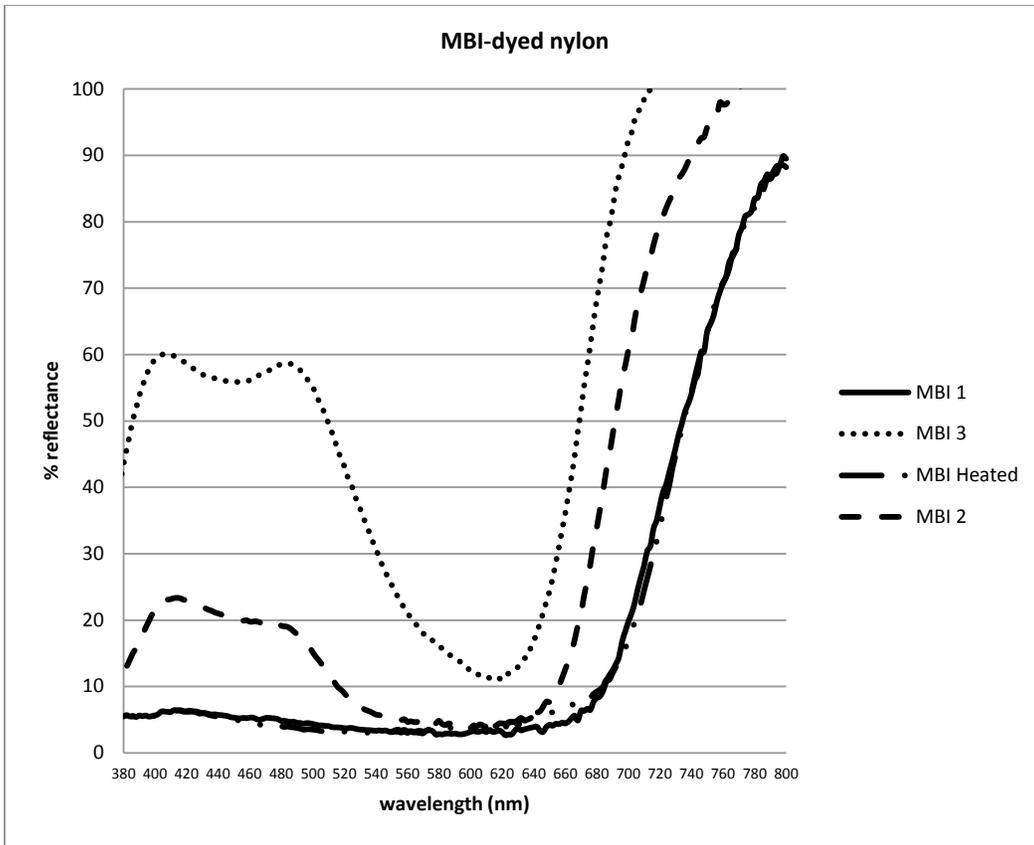
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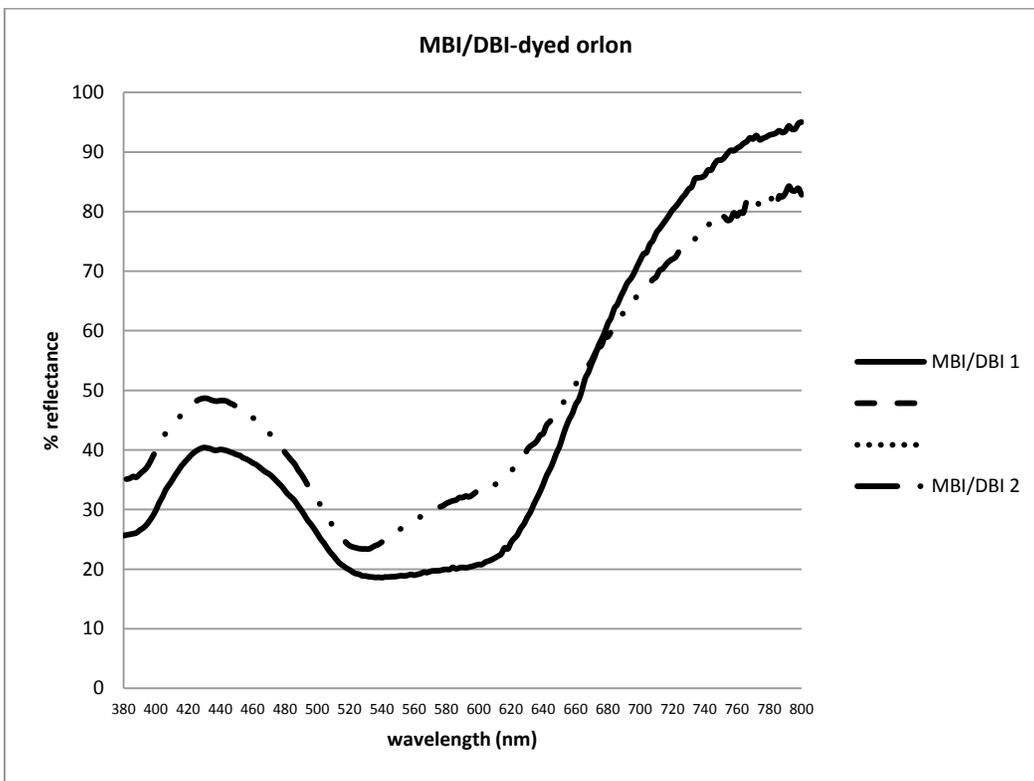
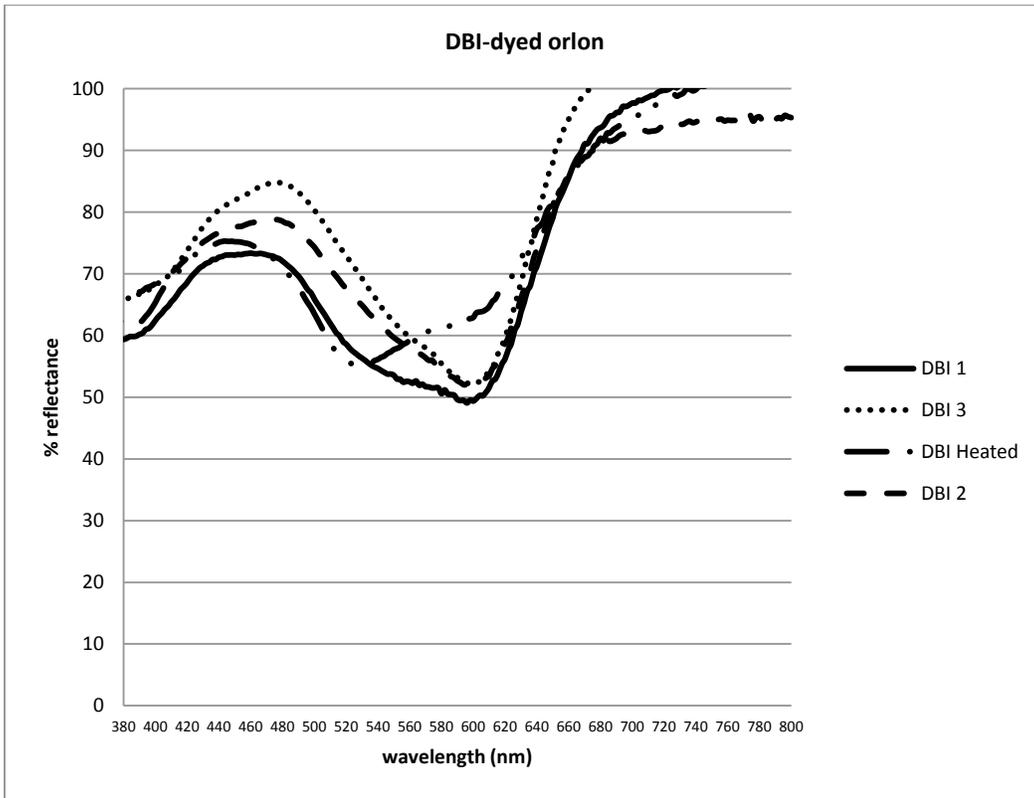


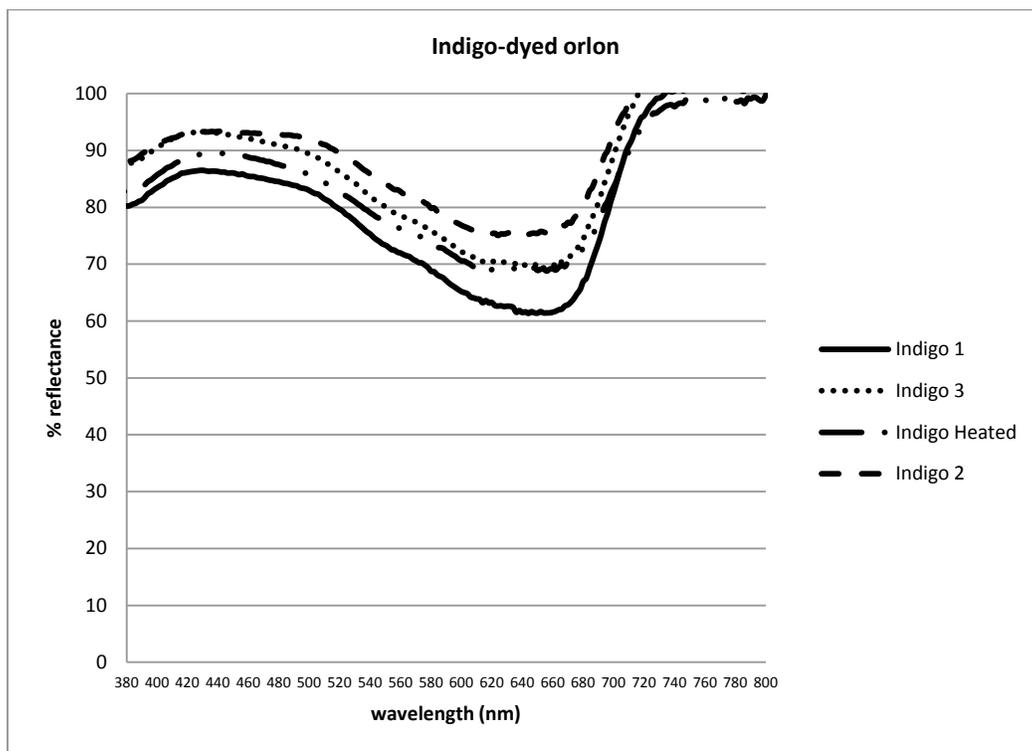
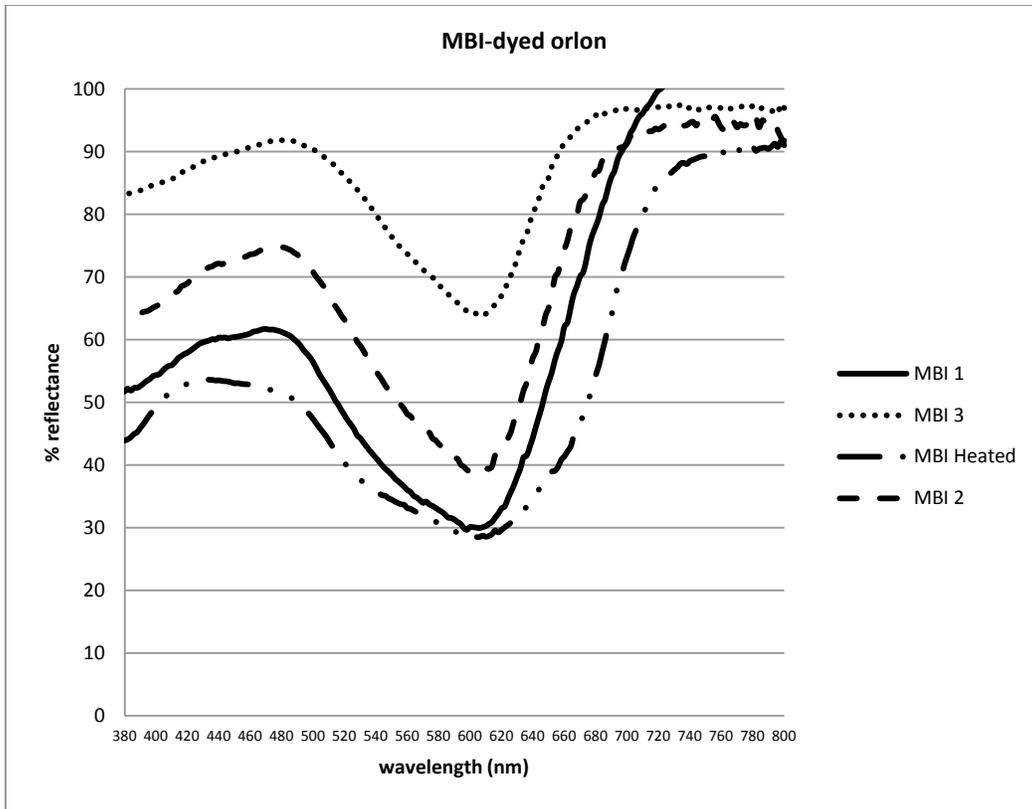
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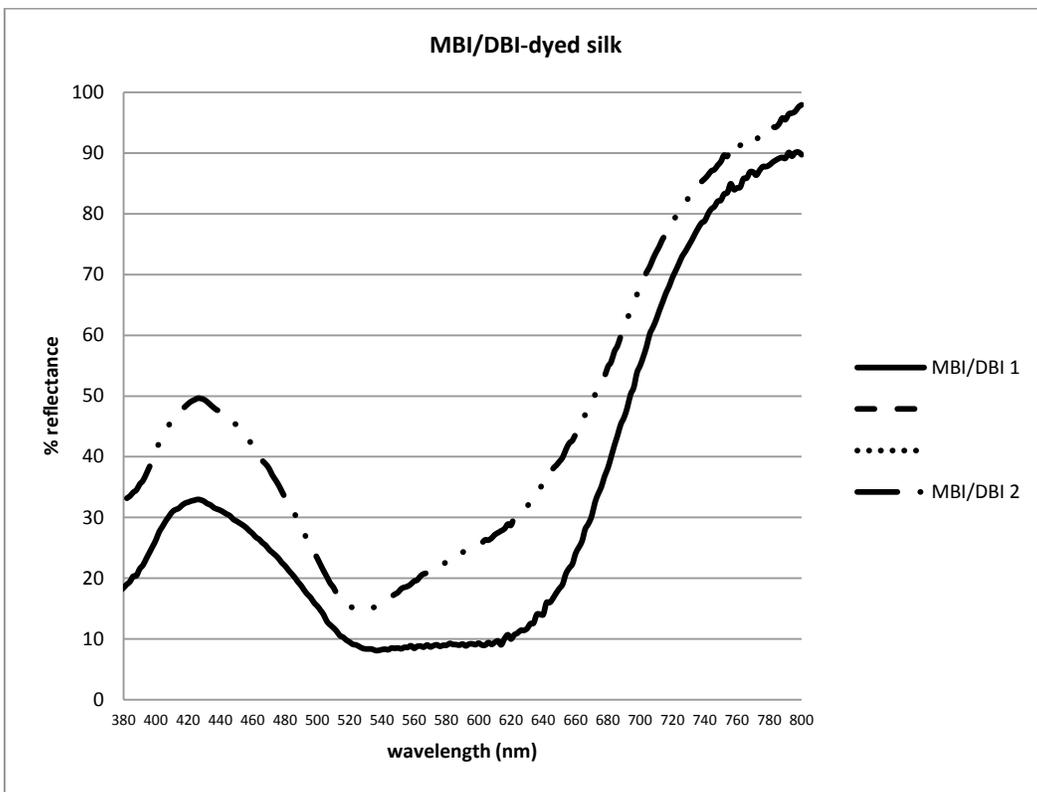
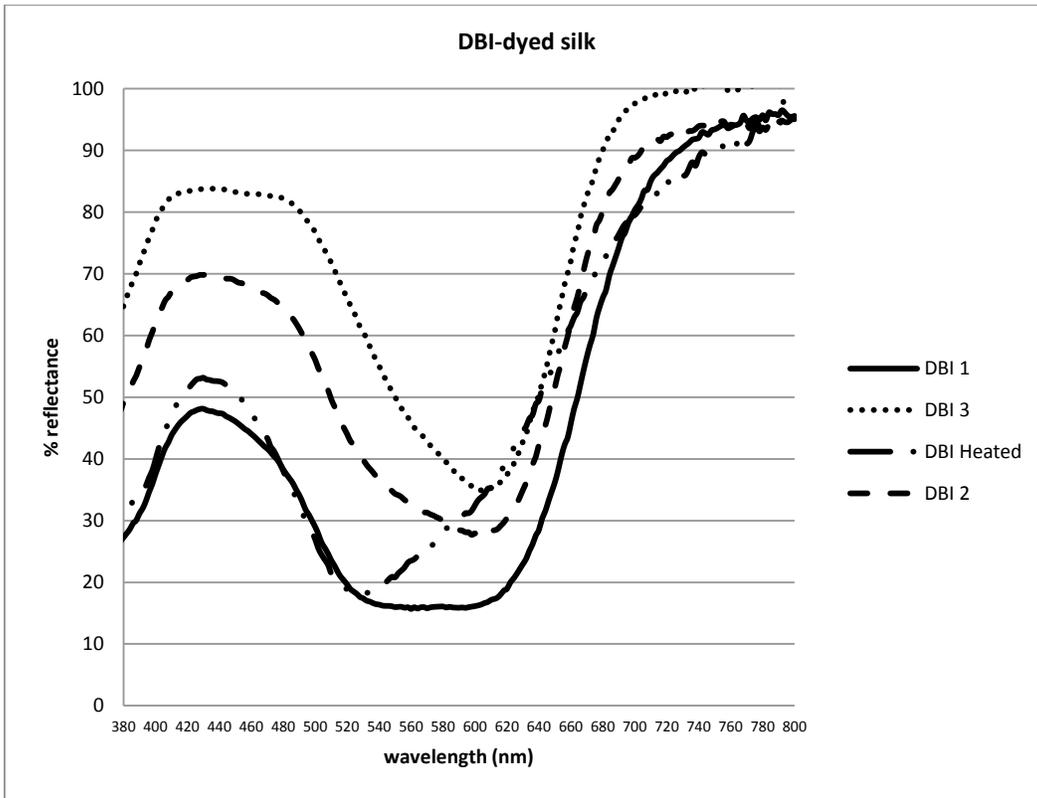


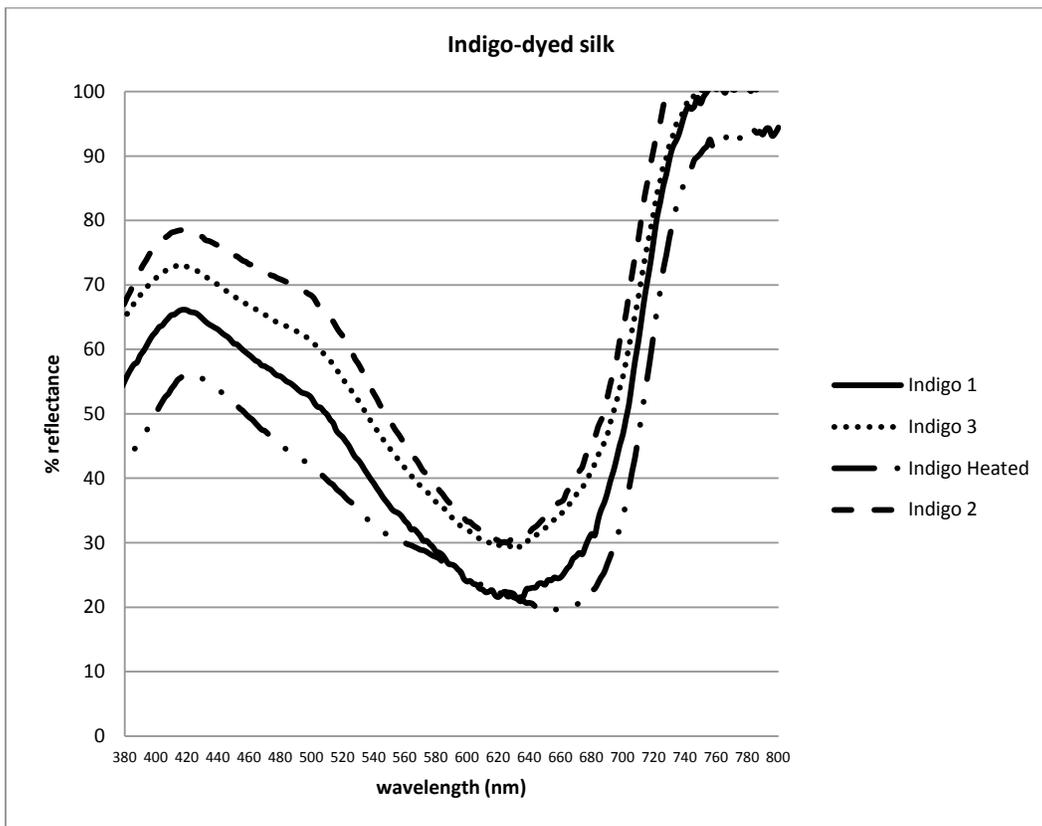
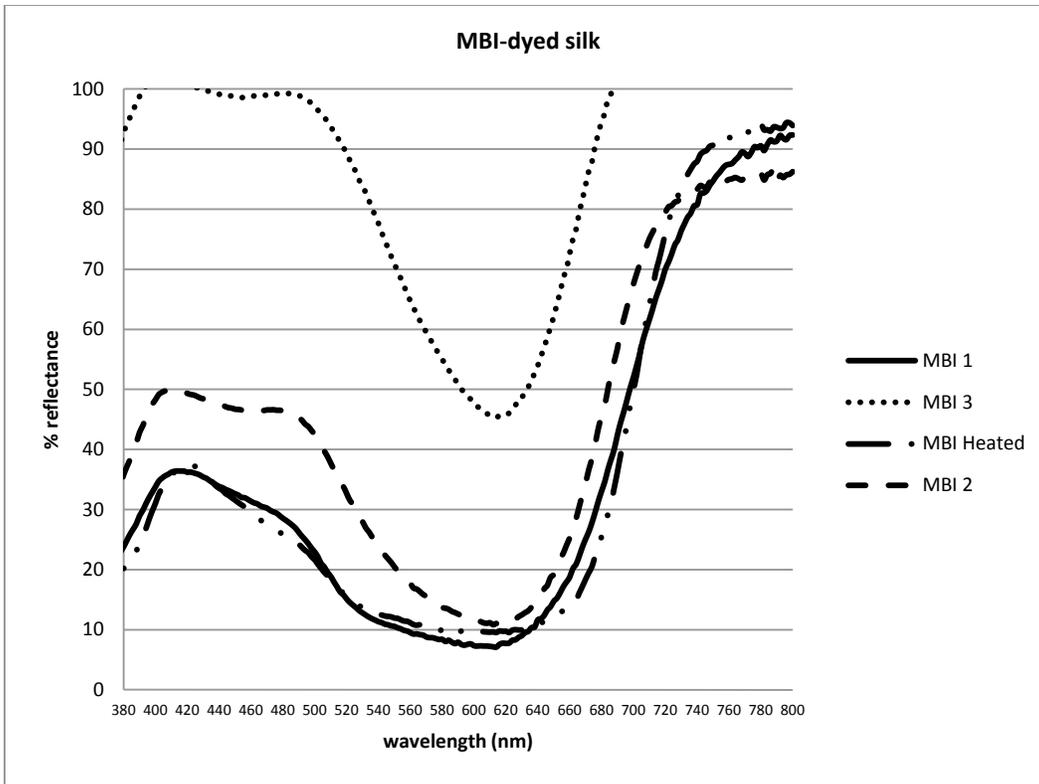
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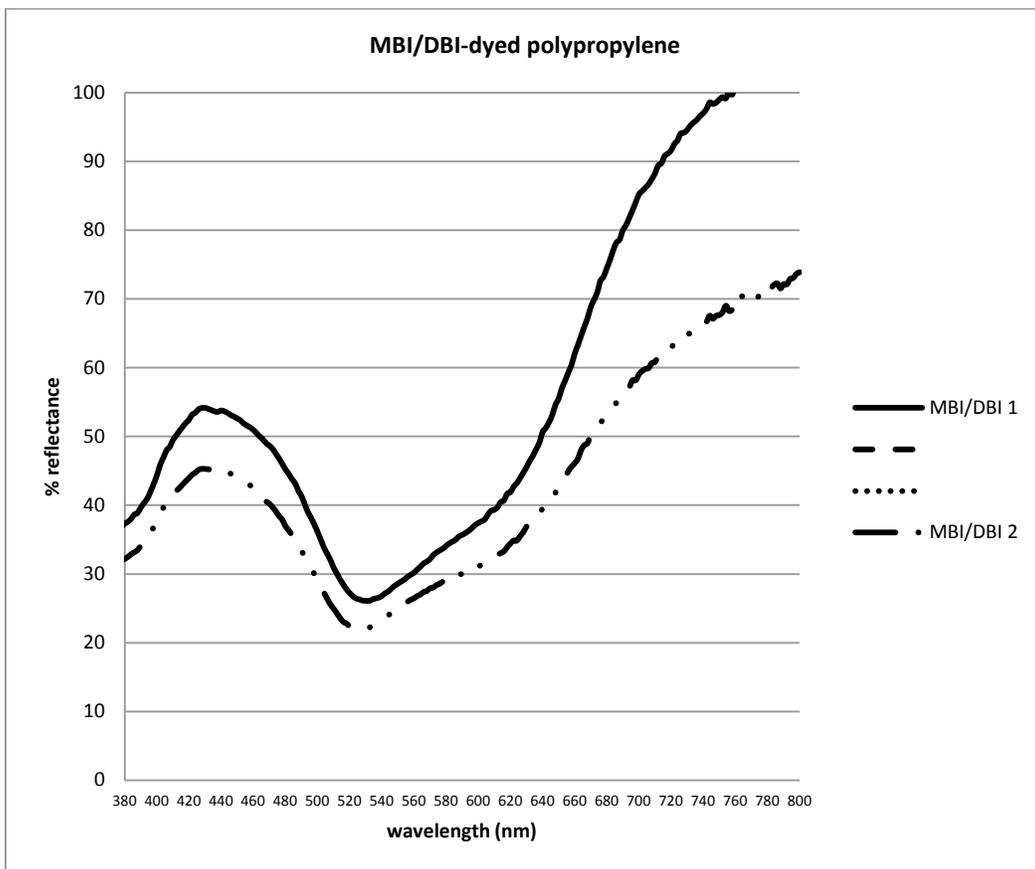
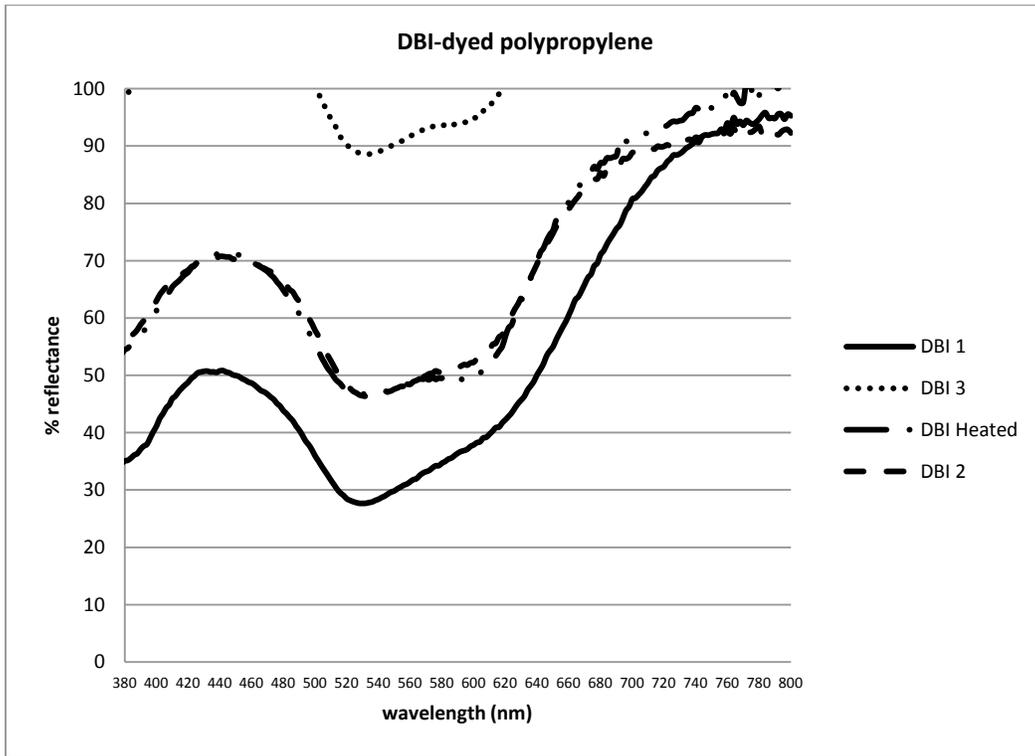


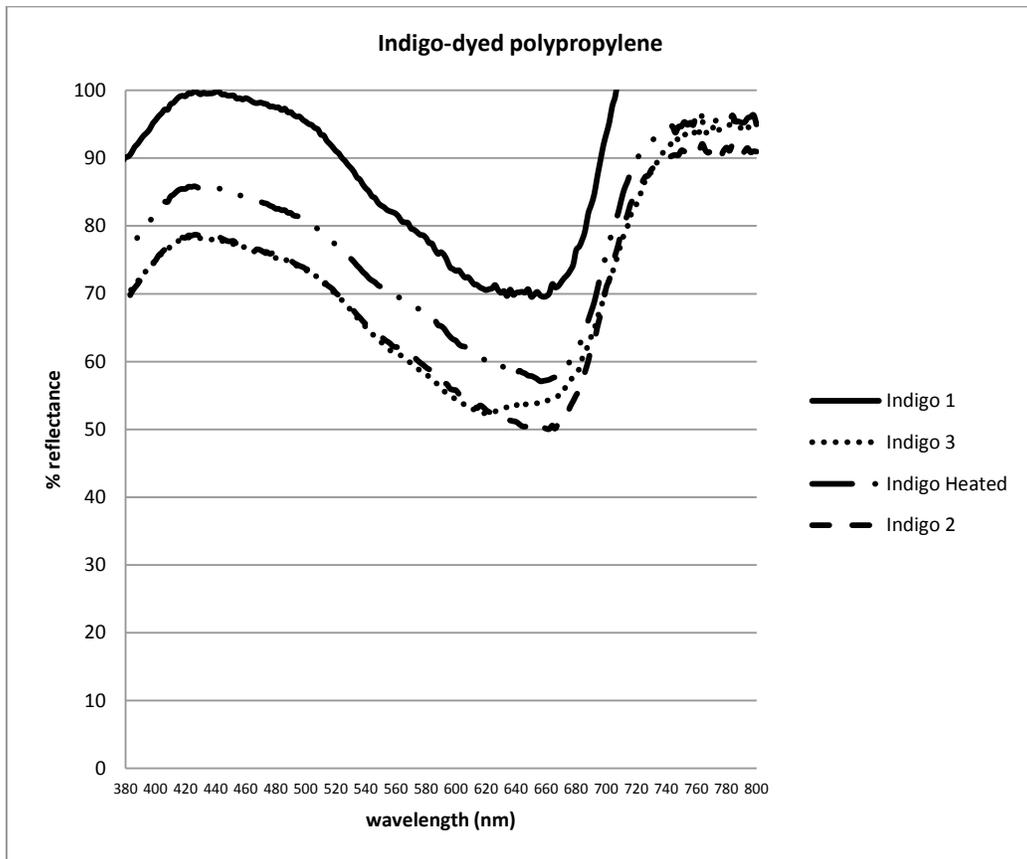
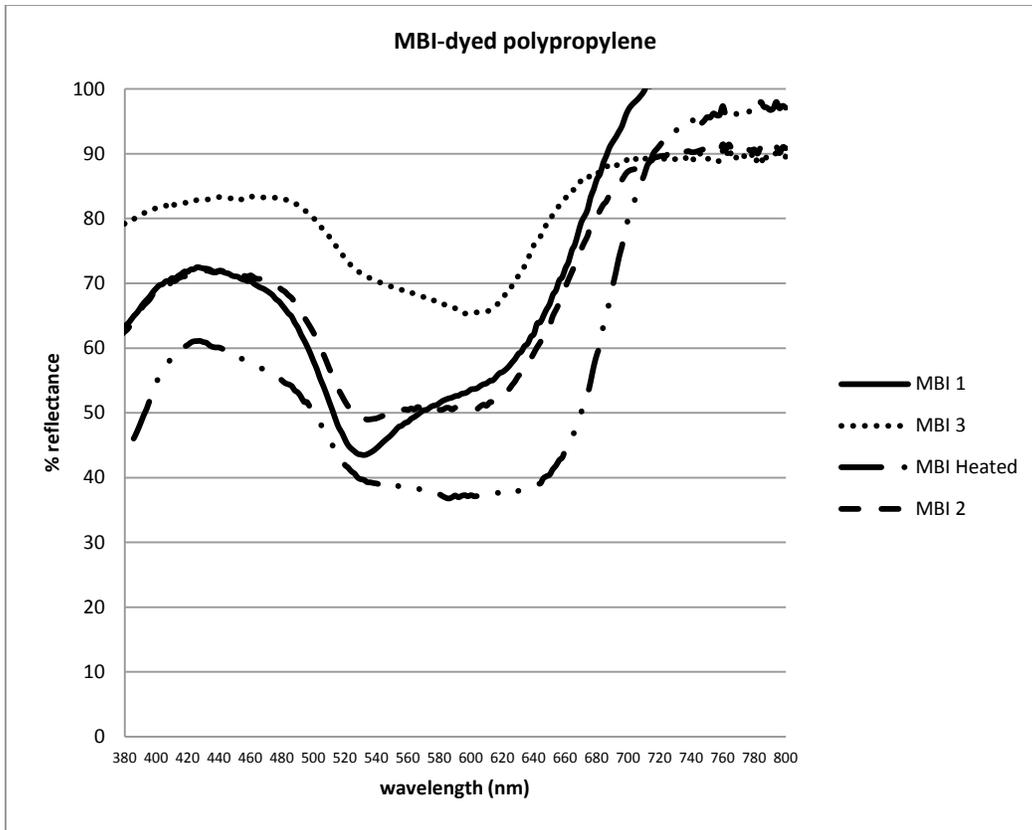
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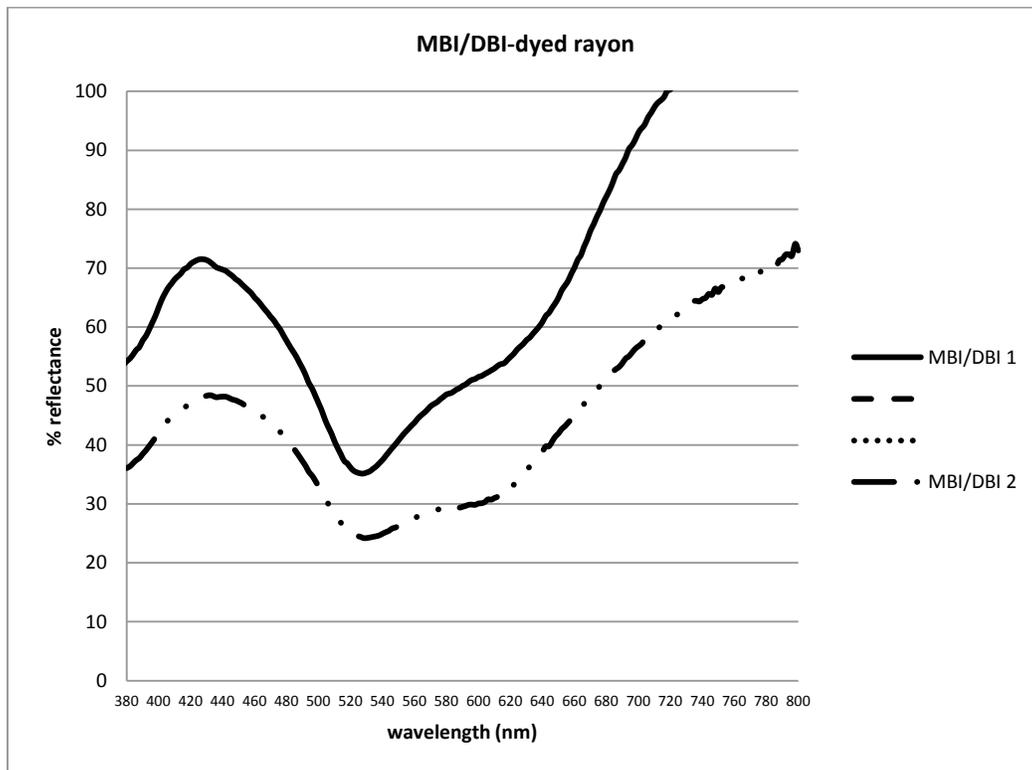
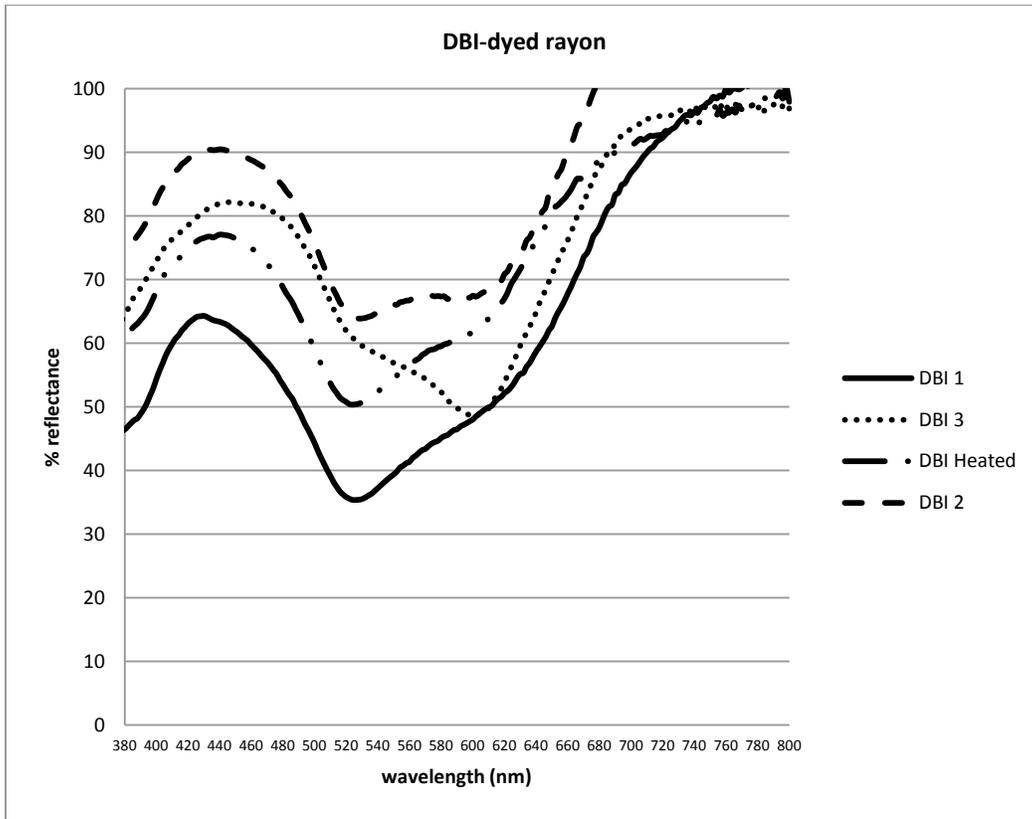


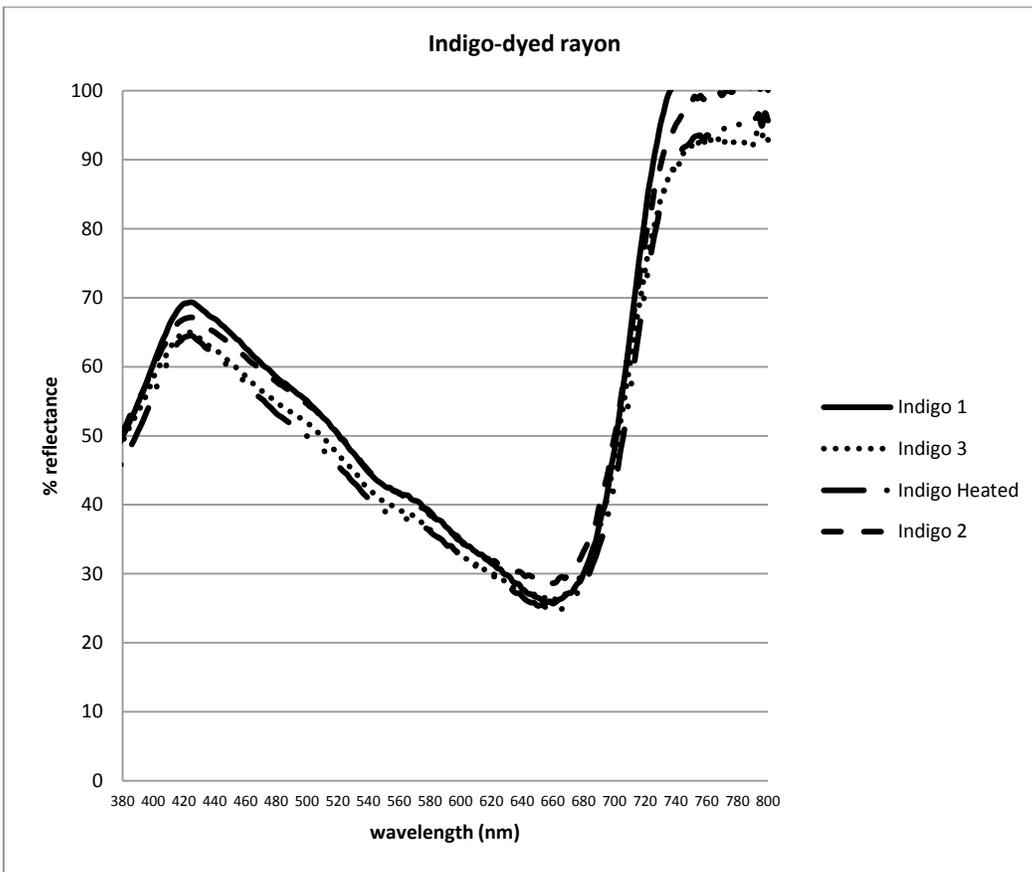
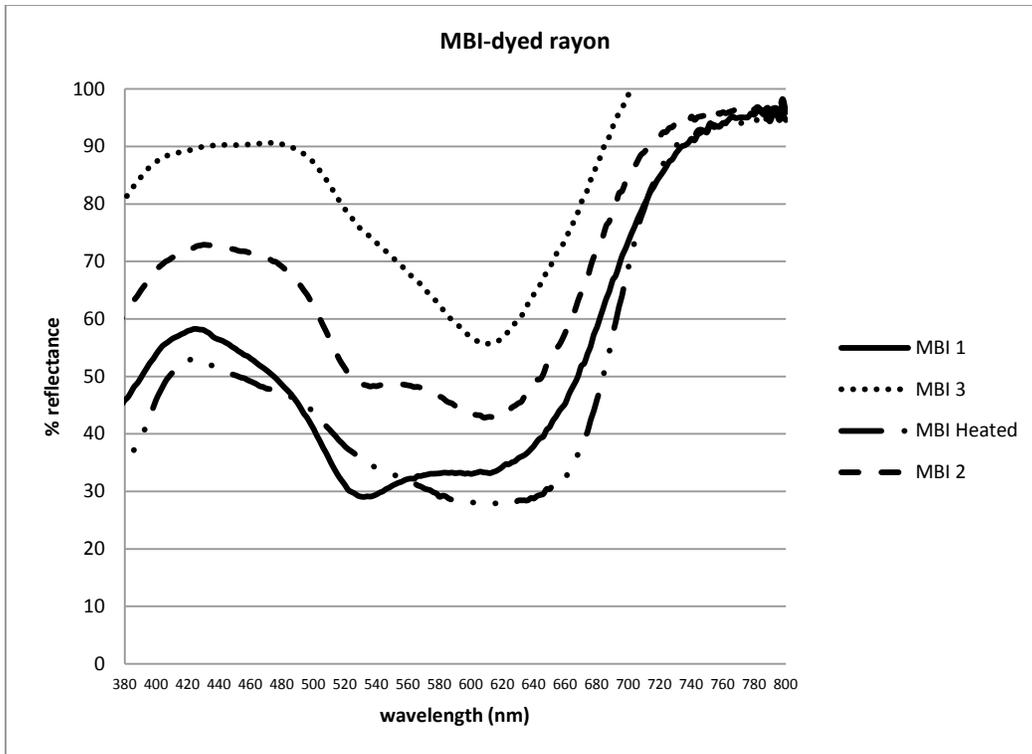
# Polypropylene





# Rayon





# Wool

