Keystone Journal of Undergraduate Research 3(1): 15-21. 2015

Fluorescence-based assessment of the curing of nail lacquers

Stephanie M. Myers
Deanna Patrushev

Faculty Mentor:
[1]Thomas A. Betts
Department of Physical Sciences
Kutztown University of Pennsylvania

ABSTRACT

The time required for a nail lacquer (or polish) to cure is an important consideration for both manufacturers and consumers. A method to assess the time required to cure thin films of nail polish is described here which is based on the viscosity-dependent fluorescence of 4-dimethylamino-4'-nitrostilbene (DMANS). DMANS fluorescence is relatively dim when dissolved in a fluid nail polish, but increases as the nail polish becomes more rigid. An inexpensive, homemade fluorimeter was constructed to measure the fluorescence of DMANS in curing nail lacquers. Curing profiles of clear top coats from three manufacturers were assessed as a function of film thickness. With a slight modification, this technique was also applied to a variety of color coats.

Keywords: curing, 4-dimethylamino-4'-nitrostilbene, DMANS, drying time, nail polish, thin film

Nail lacquer formulations are fluid – changing with customer demands as well as health and environmental considerations. While changes in formulations occur, nail lacquer must remain easy to apply, dry quickly, wear well, and remove easily. Formulation variables that impact the drying time of the lacquer include: the choice and ratios of film formers, plasticizers, and solvents (Pagano 2011). Drying, or curing, time of these thin films of nail lacquer can be assessed by several standard methods that all involve physical contact with the film such as touching the surface with a clean fingertip or cotton swab (ASTM 2009, Schlossman 1981), dragging a stylus across a drying film (ASTM 2013), or applying and brushing away small glass spheres (ISO 2010).

We have constructed an inexpensive device which provides a "hands-off" approach to assessing the curing of thin films of nail lacquer. This method relies on the viscosity-dependent fluorescence of 4-dimethylamino-4'-nitrostilbene (DMANS, Figure 1). The fluorescence process begins when a molecule absorbs light, promoting electrons from a lower energy level (the ground state) to a higher energy level (an excited state). As excited electrons relax back to the ground state, energy released as light is called fluorescence. Alternate, nonradiative pathways from the excited to ground states can occur without emission of light, and will result in diminished fluorescence intensity.

In the ground state, DMANS exists as a nearly planar structure (Singh et al. 2013). Upon excitation in highly viscous or rigid media, DMANS maintains its essentially planar excited state which can fluoresce brightly. However, in fluid media, the excited state of DMANS can twist in such a way to foster charge transfer between the electron donor portion (dimethylamine) and the electron acceptor portion of the molecule (nitrophenyl). This twisted intramolecular charge transfer (TICT) state provides a nonradiative pathway to the ground state avoiding the fluorescence pathway, thereby reducing the fluorescence intensity in fluid media (Lapouyade 1993).

Researchers have proposed several different twisting mechanisms for formation of the TICT state. Complete neglect of differential overlap/ spectroscopic (CNDO/S) calculations in the gas phase (Rettig, et al. 1992) and selective bridging (Lapouyade 1993) were used to conclude that TICT formation in DMANS is the result of twisting

[1]Corresponding author email: betts@kutztown.edu

of the nitro group (about bond 1). Coherent antiStokes Raman spectroscopy also suggests rotation of the nitro group (Oberlé et al. 2000). Yang, et al. (2004) proposed that twisting of the N,N-dimethylaniline group (about bond 4) is responsible for the excited-state TICT formation. Farstdinov and Ernsting (2002) used semiempirical calculations to support TICT formation by twisting of the nitrophenyl group (about bond 2) which was also supported by the femtosecond transient absorbance and DFT (density functional theory) and TDDFT (time dependent DFT) calculations by Singh, et al. (2013). While alternate theories exist regarding the specific twisting motion that leads to the TICT state, the result is a probe whose fluorescence depends on the viscosity of its surroundings.

When DMANS is dissolved in a nail lacquer the fluorescence should remain dim as long as the lacquer is fluid and allows twisting in the excited state. As the nail lacquer cures, the viscosity of the thin film increases, restricting the twisting of the excited DMANS, causing an increase in fluorescence to occur from the planar singlet excited state.

We describe here a light emitting diode (LED)-based, filter fluorimeter that is capable of making fluorescence measurements of DMANS dissolved in nail lacquers on a horizontal surface. This method provides an inexpensive, hands-off means to follow the curing process of nail lacquers. This device is suitable for evaluating the curing of both top and color coats.

METHODS

Reagents and Sample Preparation

Five microliters of a 1.2 x 10^{-3} M solution of DMANS (Fluka, ≥ 99.8% purity, CAS 2844-15-7) in dichloromethane (EMD Chemicals, CAS 75-09-2) was deposited on a microscope slide, and the solvent was allowed to evaporate, and the slide was tared. Between 0.01 to 0.05 grams of nail lacquer were applied to the slide over a 1.5 cm x 1.5 cm area with swirling to dissolve the previously deposited DMANS. The mass of the nail lacquer was measured immediately after deposition and swirling, then the microscope slide was promptly placed under the LED-based fluorimeter, and the entire apparatus was covered with a light-tight box. The

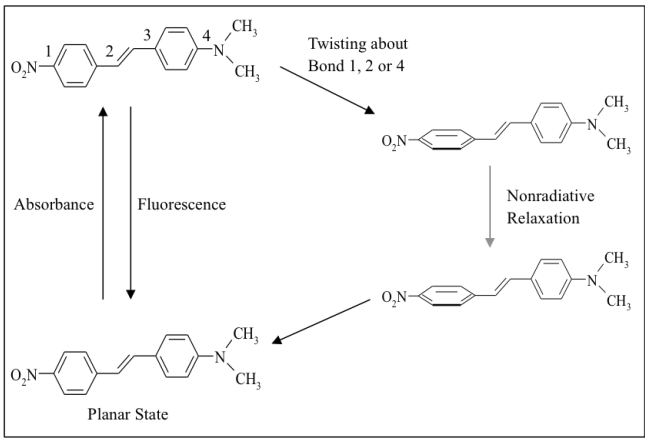

Figure 1: Explanation of the decrease in fluorescence as a result of the twisted intramolecular charge transfer (TICT) formation in 4-dimethylamino-4'-nitrostilbene (DMANS).

intensity of DMANS fluorescence was recorded as the nail lacquer cured. The time delay between the initial deposition of nail lacquer and measurement of the first intensity was consistently within 12-15 seconds.

Apparatus

The homemade LED-based fluorimeter (Figure 2) was machined from a small block of Delrin® acetal resin (3.5 cm x 2 cm x 7 cm), and includes a blue light emitting diode (T-1¾ package, 15° viewing angle, Super Bright LEDs Inc., St. Louis, MO), a 530-nm long pass filter (1-inch diameter, Edmond Optics, Barrington, NJ), and a Hamamatsu silicon photodiode (S1336-44BK). The LED was angled at 45° relative to the detector, and threaded bolts were used as legs to adjust the height of the device above the sample.

A blue, 470-nm LED excitation source was chosen because of its spectral overlap with the excitation wavelength of DMANS. A 530-nm long-pass filter was used to reject scattered light from the blue LED while allowing the orange fluorescence of DMANS around 630 nm to reach the photodiode detector.

The LED excitation source was powered by a 9-V battery through a variable resistor to allow control of the LED brightness (Figure 2). The same 9-V battery was used to supply an operational amplifier circuit based on a CA 3240 op amp (Figure 2) to amplify the signal from the silicon photodiode. The amplified signal from the detector was collected using a low-cost, 14-bit, USB, multifunction data

acquisition device (NI USB-6009, National Instruments). Software written in LabView 2013 (National Instruments) was used to collect, average, store and display fluorescence intensity measurements versus time. During the evaluation of clear nail lacquers continuous LED excitation was used, and the fluorescence intensity was averaged for 10 seconds once each minute. For colored nail lacquers the LED was pulsed on just long enough to make a measurement (about 3 seconds) each minute.

The initial intensity recorded was used to represent the fresh nail lacquer (0 % dry). Over time during the curing process the fluorescence intensity continually increased until it reached a relatively stable maximum. This maximum intensity was used to represent a completely cured nail lacquer (100% cured). The % cure was determined as the fraction of the fluorescence intensity between the minimum and maximum for each run:

$$\%\ Cure = \left(\frac{Int - Min\ Int}{Max\ Int - Min\ Int}\right) x100$$

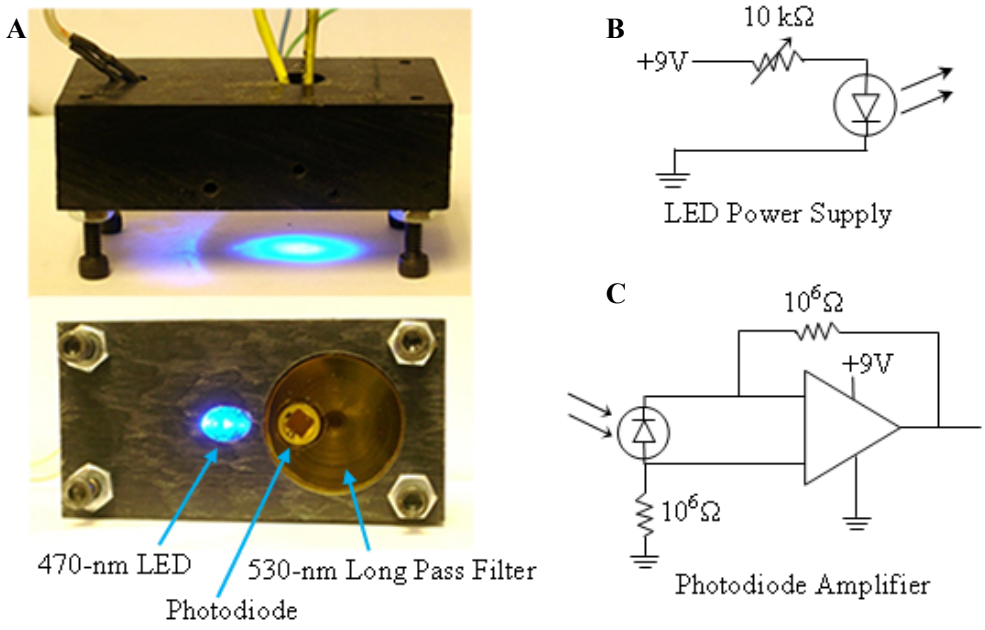

Figure 2: A) Side and bottom views of the LED-based horizontal fluorimeter. B) Power supply circuit for the LED. C) Operational amplifier circuit for silicon photodiode detector**.**

RESULTS

Figure 3 A depicts the measured raw fluorescence intensity of DMANS as measured by the amplified photodiode in three repeated trials for the curing of 0.024 g of Orly In A Snap fast drying nail lacquer as a function of time. The low initial fluorescence intensity resulted from DMANS being able to twist in the excited state to form the TICT state and relax without emitting light because of its fluid surroundings. The increase in DMANS fluorescence intensity with time as the thin film cured was due to DMANS being trapped in the planar excited state. The raw fluorescence data does not appear to be reproducible due to differences in casting the thin film. Orientation of the sample under the LED fluorimeter and distribution of DMANS throughout the thin film are two likely causes of irreproducibility in the raw fluorescence intensity. Normalizing based on the spread of intensity measurements as % Cure for each run provided a convenient means to compare data sets collected under slightly different experimental circumstances (Figure 3 B).

Curing profiles were assessed for three clear top coats from three different manufacturers as a function of film thickness (Figure 4). Attempts to measure film thickness using a set of calipers were thwarted by a lack of precision and resolution. While absolute film thicknesses were unknown, relative film

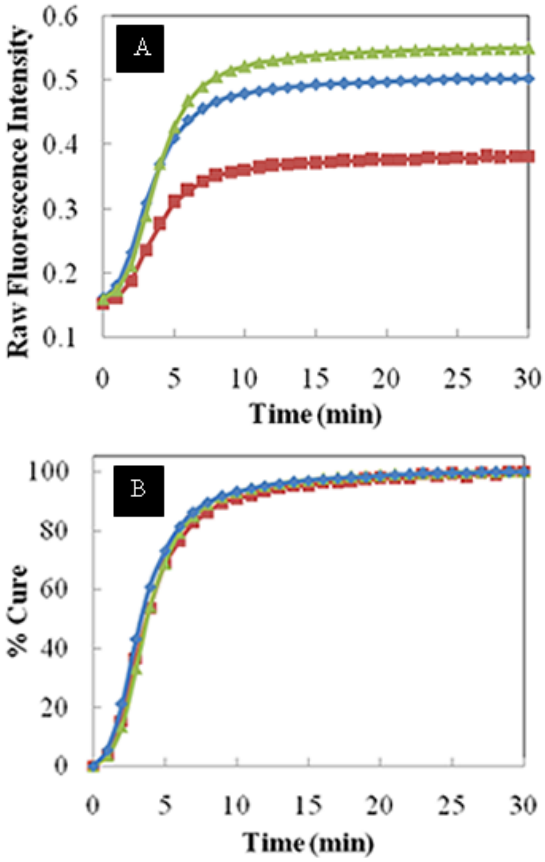

Figure 3: A) Raw fluorescence intensity of three repeated trials of 0.024 g of Orly In A Snap fast drying top coat. B) The same three repeated trials plotted in a normalized fashion as % Cure.

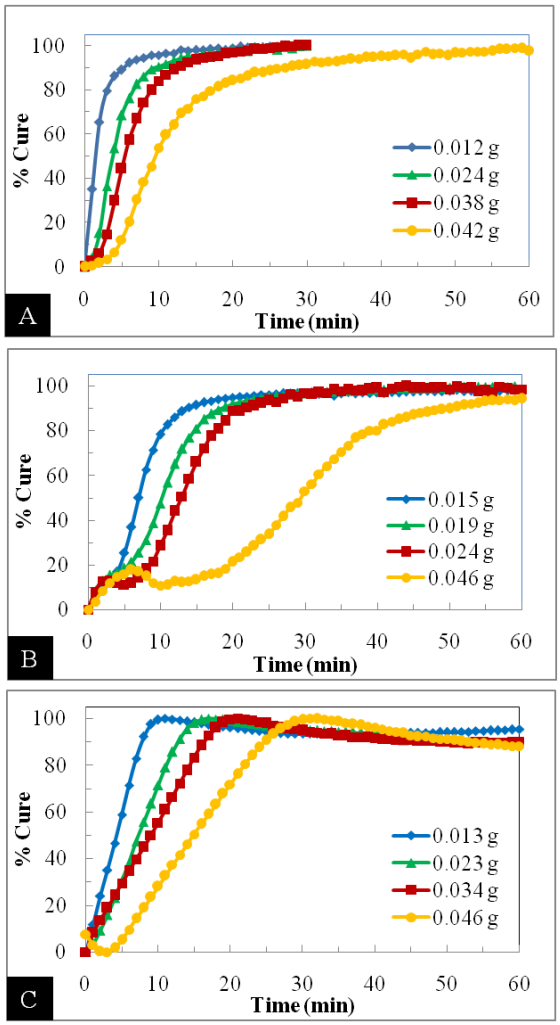

Figure 4. Curing profiles of three different clear nail lacquers as film thickness varied. Different masses of each nail lacquer were spread over a consistent 1.5 cm x 1.5 cm area to vary thickness. Panel A contains curing profiles from Orly In a Snap fast-drying clear top coat. Panel B contains curing profiles for Seche Vite clear top coat. Panel C contains curing profiles for Wet N Wild clear nail lacquer.

thickness was varied by controlling the mass of wet nail lacquer spread over a consistent area of 2.25 cm^2.

As expected, for each sample the curing time increased with increasing thickness. The Orly fast-drying top coat depicted in Figure 4A was indeed determined to be the fastest drying product of the three clear lacquers tested. The shape of the curing profile remained fairly consistent as film thickness increased. This was not the case for the Seche Vite clear top coat (Figure 4B) where the thickness of the nail lacquer film dramatically influenced the shape of the curing profile. This could have been due to the presence of several solvents evaporating at different rates. With thicker samples of this particular nail lacquer, the fast evaporating solvent may have created a skin over the sample that slowed the evaporation of additional solvent. When DMANS was used to assess the curing of Wet N Wild clear nail lacquer (Figure 4C) there was a slight decrease in the fluorescence intensity after a peak occurred.

When the same instrument conditions that were used to assess clear top coats were applied to colored nail lacquers (namely, bright continuous LED excitation), this decrease in fluorescence after the maximum was exacerbated. The trace in Figure 5 obtained with bright, continuous LED excitation shows an increase in DMANS fluorescence intensity over the first 7.5 minutes followed by a dramatic decrease well below the initial intensity as curing continued in a sample of

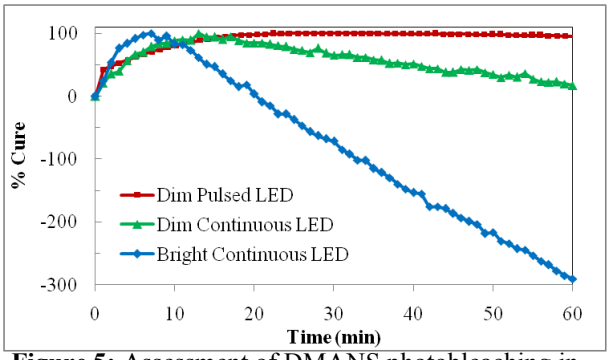

Figure 5: Assessment of DMANS photobleaching in the curing of 0.025 g China Glaze Re-Fresh Mint (green) nail lacquer when excitation was from a bright continuous LED, a dim continuous LED and a dim pulsed LED.

China Glaze Re-Fresh Mint creating an artificially negative % Cure.

If the cause of the decreasing DMANS fluorescence at longer times was due to photobleaching (degradation as a result of impinging light intensity), then decreasing the intensity of the LED excitation source should mitigate degradation. The trace in Figure 5 corresponding to the dim, continuous excitation was obtained by decreasing the intensity of the LED using the variable resistor in the LED power supply. Decreasing the intensity of the excitation beam resulted in a smaller overall decrease after the maximum intensity was reached suggesting that the cause of the decrease was due to destruction of DMANS by photobleaching. In order to alleviate as much photobleaching as possible, LabView was used to turn on the LED excitation source for only three seconds each minute, just long enough to allow the LED output to stabilize and make a measurement. Keeping the LED off the other 57 seconds each minute dramatically reduced the extent of photobleaching (Figure 5, Dim Pulsed LED trace).

One additional consequence of photobleaching apparent in Figure 5 was that photobleaching caused the % Cure peak to skew to earlier times. This was a result of the raw peak intensity arriving sooner due to the degradation of fluorescence during the curing process. Cure times for samples that cause photobleaching must be interpreted with caution.

The pulsed LED technique was used to obtain curing profiles for several yellow (Orly Hook Up and China Glaze Solar Power), pink (Orly Basket Case and China Glaze Laced Up), teal (China Glaze For Audrey) and green (China Glaze Re-Fresh Mint) nail lacquers (Figure 6). The pulsed LED technique was also applied to one of the clear topcoats evaluated in Figure 3 (0.024 g Orly In a Snap fast drying top coat), and the results were consistent with continuous illumination.

Nearly all of the color coats tested displayed similar curing profiles with the exception of Orly Basket Case where photobleaching was still a problem even with the pulsed excitation source. As seen in Figure 5, photobleaching caused a shift in the curing profile to earlier times.

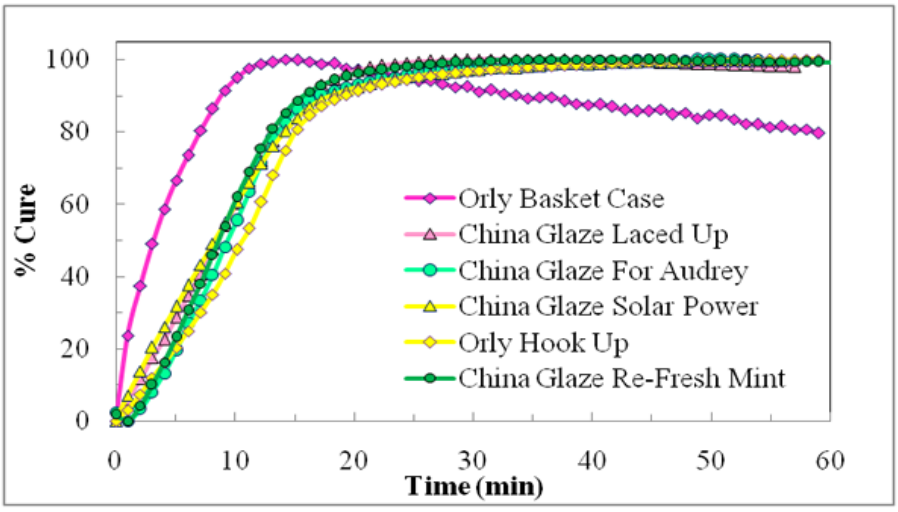

Figure 6: Curing profiles for 0.025 g of various color coats using a pulsed LED excitation source.

DISCUSSION

The horizontal arrangement of this LED-based fluorimeter allowed for the measurement of fluorescence on cast films without interference from gravity. When used to record the fluorescence of DMANS in curing nail lacquers, relatively large changes in fluorescence intensity enabled the assessment of curing progress without physically touching the surface. The method was inexpensive, experimentally straight-forward, and reproducible. Normalization with respect to the lowest and highest recorded fluorescence intensities in each profile was essential for reproducibility in assessing the curing of thin films of nail lacquer.

Our fluorescence-based approach was capable of detecting differences in curing profiles with changes in brands and thickness. These differences in the fluorescence-based curing profiles provided more information regarding the chemistry of the curing process than the standard contact-based methods (ASTM 2009, ASTM 2013 and ISO 2010).

This method was applicable to both clear coats and color coats. Degradation of the fluorescent dye, DMANS, resulting from the impinging intense, blue light, was more significant in color coats than in clear coats. Photobleaching of DMANS has been observed when it has been incorporated in polymethylmethacrylate (Galvan-Gonzalez et al 1999, Shan et al. 2000, Galvan-Gonzalez et al. 2003). It has also been shown that the addition of a photosensitizer can increase the rate of the photobleaching process (Zyung et al. 1994). The colorants in these heavily pigmented nail polishes could act as photosensitizers, absorbing some of the energy from the impinging radiation and transferring that energy to a mechanism that encourages degredation of DMANS. Even though we do not fully understand the mechanism of photobleaching in colored nail polishes yet, we were able use the flexibility of the LabView software to minimize photodegredation by pulsing the LED on only when a fluorescence measurement was being made.

We believe that the "hands-off", fluorescence-based approach to the determination of nail polish curing deserves consideration as a complement to currently acceptable, contact-based methods of assessing cure times of thin films. As nail polish formulations continue to evolve, a non-contact, fluorescence-based approach may provide additional insight into the curing process.

LITERATURE CITED

ASTM D1640-03. 2009. Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature, ASTM International, West Conshohocken, PA.

ASTM D5895-13. 2013. Standard Test Methods for Evaluating Drying or Curing During Film Formation of Organic Coatings Using Mechanical Recorders, ASTM International, West Conshohocken, PA.

Farztdinov, V.M. and N.P. Ernsting. 2002. Solvent dependence of structure and electronic properties in the ground and first excited singlet state of 4-dimethylamino-4'-nitostilbene (DANS) – semiempirical calculations. *Chemical Physics* 277(3): 257-270.

Galvan-Gonzalex, A., M. Canva, and G.I. Stegeman. 1999. Local and external factors affecting the photodegredation of 4 N,N'-dimethylamino-4'nitrostilbene polymer films. *Applied Physics Letters* 75(21): 3306-3308.

Galvan-Gonzalex, A., K.D. Belfield, G.I. Stegeman, M. Canva, S.R. Marder, K. Staub, G. Levina, and R.J. Twieg. 2003. Photodegredation of selected π-conjugated electro-optic chromophores. *Journal of Applied Physics* 94(1): 756-763.

ISO 9117-3. 2010. Paints and Varnishes – Drying Tests – Part 3: Surface-drying test using ballotini. International Organization for Standardization, Geneva, Switzerland.

Lapouyade, R., A. Kuhn, J.F. Letard, and W. Rettig. 1993. Multiple relaxation pathways

in photoexcited dimethylaminonitro- and dimethylaminocyano-stilbenes. *Chemical Physics Letters* 208(1-2): 48-58.

Oberlé, J., E. Abraham, G. Jonususkas, and C. Rulliere. 2000. Study of the intramolecular charge-transfer (ICT) process in 4-dimethylamino-4'-nitrostilbene by picoseconds time-resolved CARS. *Journal of Raman Spectroscopy* 31(4): 311-317.

Pagano, F.C. 2011. A review of nail polish: the industrial cosmetic. *Cosmetics & Toiletries magazine* 126, 373-379.

Rettig, W., W. Majnez, R. Lapouyade, and F. Haucke. 1992. Multidimensional photochemistry in flexible dye systems. *Journal of Photochemistry and Photobiology A: Chemistry* 62: 415-427.

Schlossman, M.L. 1981. Techniques for evaluation of nail enamel. *Journal of the Society of Cosmetic Chemists* 32(1): 43-52.

Shan, J.-X., Q.-S. Shen, A.-H. Zhang, Z.-Q. Cao and Y.-L. Chen. 2000. Determination of the refractive index profile of a polymer waveguide by photobleaching. *Chinese Physics Letters* 17(6): 433-434.

Singh, C., R. Ghosh, R., J.A. Mondal, and D.K. Palit. 2013. Excited state dynamics of a push-pull stilbene: a femtosecond transient absorption spectroscopic study. *Journal of Photochemistry and Photobiology A: Chemistry* 263: 50-60.

Yang, J.-S., K.-L. Liau, C.-M. Wang, and C.-Y. Hwang. 2004. Substituent-dependent photoinduced intramolecular charge transfer in N-aryl-substituted trans-4-aminostilbenes. *Journal of the American Chemical Society* 126(39): 12325-12335.

Zyung, T., W.-Y.Hwang, J.-J. Kim. 1994. Accelerated photobleaching of nonlinear optical polymer for the formation of optical waveguide. *Applied Physics Letters* 64(26): 3527-3529.