



## Using polydiacetylenic microcrystals in textile as thermochromatic sensor

 Kh. El-Nagar<sup>1,\*</sup>, J. Pang<sup>2</sup>, Y. Lu<sup>2</sup> and C. J. Brinker<sup>3</sup>
<sup>1</sup>National Institute for Standards, Giza, Egypt

<sup>2</sup>Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118;

<sup>3</sup>UNM/NSF Center for Micro-Engineered Materials, The University of New Mexico, Albuquerque, New Mexico 87131.

### ARTICLE INFO

#### Article history:

Received: 17 January 2011;

Received in revised form:

25 January 2012;

Accepted: 9 February 2012;

#### Keywords

 Smart material,  
 10,12pentacosadiynoic acid,  
 Heat sensor,  
 CIE-LAB,  
 Reflection,  
 Heat sensors,  
 Smart textiles.

### ABSTRACT

This work aimed to apply a thermochromatic polymer based on 10,12-pentacosadiynoic acid (PCDA) monomer as a temperature sensor. This polymer has specific chemical structure enabling it to vary its color parameters, namely CIE L (brightness), a (red-green) and b (yellow-blue), with the temperature transitions. These color parameters were calculated in accordance to the American standard ASTM number E308-2001. All changes in the temperature were found to be easily tuned with the visual color and the color difference ( $\Delta E$ ). These changes were found to be recyclable and reversible in the studied temperature range of 25-105°C with regression factor equals unity.

© 2012 Elixir All rights reserved.

### Introduction

Smart materials and structures are the materials and structures that sense and react to environmental conditions or stimuli, such as those from mechanical, thermal, chemical, electrical, magnetic or other sources. According to the manner of reaction, they can be divided into passive smart, active smart and very smart materials. Passive smart materials can only sense the environmental conditions or stimuli; active smart materials will sense and react to the conditions or stimuli very smart materials can sense, react and adapt themselves accordingly. An even higher level of intelligence can be achieved from these intelligent materials and structures capable of responding or activated to perform a function in a manual or pre-programmed manner. Three components may be present in such materials: Sensors, actuators and controlling units. These materials and structures are becoming possible as the result of a successful marriage of traditional technology with material science, structural mechanics, sensor and actuator technology, advanced processing technology, communication, artificial intelligence, biology, etc. (Xiaoming, 2001).

All materials absorb photons of some energy. But only substances that absorb photons of visible light will have color. Molecules are very selective about what photon energies they will and will not absorb. In fact, the photon energies a molecule will absorb are so characteristic that they can be used as a 'fingerprint' to identify that molecule in a mixture. This preferential absorption can be explained by assuming that molecules have quantized energies; that is, they exist only in certain allowed energy states. Every compound absorbs a characteristic set of colors of light. This absorption spectrum is a chemical fingerprint for detecting the presence of that compound. When the compound is altered in a chemical reaction, fingerprint will change- and so the color of the reacting

mixture may change, as the reaction progresses. It is possible to have a color change without a chemical change, however, because a compound's absorption spectrum isn't the only thing that affects its color. For example, heating zinc oxide changes it from white to yellow but no real chemical change occurs. The color change is caused by holes and other defects that are created in the zinc oxide lattice as the compound is heated. On heating the chemical compound, it takes energy to break chemical bonds. And energy is released when new chemical bonds form. When the reaction involves more bond-breaking than bond making, the energy required is often absorbed from the surroundings, making them cooler. When there is more bond-making than bond-breaking, the excess energy is released, making the surroundings hotter [Lio et al., 1997; Pires et al., 2008].

Polydiacetylene (PDA) has received intensive research interest due to its unique electronic, chromatic and optical nonlinear properties that result from its extended  $\pi$  electron conjugation and backbone alignment. (Mino et al., 1991; Angkaew et al., 1994; Jonas et al., 1999; Okada et al., 1998). Most PDA materials show irreversible or reversible thermochromatism when subjected to thermal stimuli, (Ahn et al., 2003; Yuan et al., 2004; Lu et al., 2001; Yang et al., 2003; Tachibana et al., 2001), which is of considerable interest for application as thermal sensors. Recently, the chromatic reversibility of PDA has been achieved through enhanced intermolecular interactions of diacetylene derivatives by hydrogen bonding (Jonas et al., 1999; Ahn et al., 2003; Yuan et al., 2004) or electrostatic interactions (Hang et al., 2005). This allows the supramolecule assemblies to restore their original molecular conformation after the removal of thermal stimuli resulting into completely reversible thermochromatism. Very recently, (Jiebin et al., 2006) we found that topochemically

Tele:

 E-mail addresses: [khnagare\\_nis@yahoo.com](mailto:khnagare_nis@yahoo.com)

© 2012 Elixir All rights reserved

polymerized polydiacetylene sodium salt (PDA-Na) undergoes unique sequential thermochromatic transitions, i.e., irreversible pink to blue, reversible blue to red, and finally irreversible red to orange, in response to thermal stimuli from room temperature to above 130 °C. In the current work, we are trying to explore in detail on the potential applications of the materials as thermal sensors.

This work aimed to apply the previously prepared polydiacetylene polymeric materials as thermochromatism sensor as when it was subjected to thermal stimuli, it gives different color parameters (CIE L, a and b). These changes in the color parameters were correlated to the temperature stimulations. Also the color difference ( $\Delta E$ ) was correlated to the temperature to gives better color temperature scale and examine its linearity.

#### Materials and Methods

**Materials.** Sodium hydroxide (NaOH, CAS Number 1310-73-2) and Tetrahydrofuran (THF, CAS Number 109-99-9) were purchased from Aldrich Chemicals, USA. 10,12-pentacosadiynoic acid (PCDA, CAS number 66990-32-7,  $\text{CH}_3(\text{CH}_2)_{11}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$ ) was purchased from GFS Chemicals, USA. PCDA was purified by filtration of a PCDA/THF solution to remove any oligomer or polymer.

**Synthesis.** For a typical synthesis procedure, (Jiebin et al., 2006) 0.072 g purified colorless 10,12-pentacosadiynoic acid (PCDA) monomer was dissolved in a mixture of 4.371 g deionized water, 1.190 g of 1 mol/L NaOH aqueous solution, and 0.279 g tetrahydrofuran (THF) to achieve a clear homogeneous solution after *ca.* 30 min of vigorous stirring. The molar ratio of PCDA:NaOH:H<sub>2</sub>O:THF was kept at 1:6:1600:20-40. After 2-4 hours of continuous stirring at room temperature (*ca.* 25 °C), sodium 10,12-pentacosadiynoate (PCDA-Na) microcrystals began to precipitate from the solution by self-assembly. The mixture was covered by aluminum foil during the crystallization process to prevent polymerization due to light exposure. After 24 h of stirring, the cloudy mixture containing white precipitated crystals was cast on glass slides and dried at room temperature. The red polydiacetylene sodium salt (PDA-Na) microcrystals were formed via topochemical 1,4-addition polymerization of the diacetylenic units by exposure to room light in the laboratory for *ca.* 3 days at room temperature.

The resulted PDA-Na was mixed with polyacrylate (PA) polymer in the presence of ammonium sulphate (AMS). The weight percentage of the PDA-NA: MTB: AMS was kept at 10:100:25. The mixture was stirred mechanically at 50 rpm (low rpm to avoid the degradation of the binder molecules) for 30 minutes to obtain the highest homogeneity. The cellulosic fabric was coated with this mixture and padded to remove excess liquid. The wetted fabric was dried at room temperature and exposure to the artificial day light at room temperature and finally cured at 80 for 12 minutes (El-Nagar et al., 1998).

#### Testing and analysis

The structure and composition of the PDA-Na microcrystals were characterized in detail as reported recently. (Jiebin et al., 2006).

**Color Measurements and calculations:** The reflection spectroscopy measurement was conducted on a piece of glass slide and cotton fabric coated with a very thin layer of crystal samples using a Perkin Elmer Lambda 45 double beam UV-VIS spectrophotometer that attached with reflectance accessory. The samples were heated by a flow of water with tunable temperature and the temperature of the samples was monitored by a thermocouple meter.

**Tristimulus values X, Y and Z** (ASTM E308-9: 2001; Hunt et al., 1999): They are derived from the reflection spectra in the visible wavelength range (380-780 nm) and the spectral color tristimulus values (color matching functions)  $x_{10}$ ,  $y_{10}$  and  $z_{10}$  of the CIE 1931 standard (2°) observer, at 5 nm intervals from 380 to 780 nm. The values of X, Y and Z calculated using the following equations:

$$X = K \cdot \sum_{\lambda} R(\lambda) \cdot S(\lambda) \cdot x_{10}(\lambda) \cdot \Delta\lambda \quad \text{-----(1)}$$

$$Y = K \cdot \sum_{\lambda} R(\lambda) \cdot S(\lambda) \cdot y_{10}(\lambda) \cdot \Delta\lambda \quad \text{-----(2)}$$

$$Z = K \cdot \sum_{\lambda} R(\lambda) \cdot S(\lambda) \cdot z_{10}(\lambda) \cdot \Delta\lambda \quad \text{-----(3)}$$

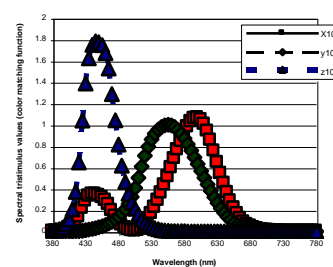
where  $R(\lambda)$  = Reflectance, transmittance or radiance factor

$S(\lambda)$  = Relative spectral power of a CIE standard illuminant, and

$x_{10}$ ,  $y_{10}$  and  $z_{10}$  = Color matching functions of CIE 1931 standard (2°) observer (Figure 1)

The summation is carried out over the entire wavelength region in which the color-matching functions are defined. The normalizing factor 'k' is defined as:

$$K = 100 / \sum_{\lambda} S(\lambda) y_{10}(\lambda) \Delta\lambda \quad \text{-----(4)}$$



**Figure 1 : Spectral tristimulus values (color matching function) x,y, z of the CIE 1931 standard (2°) observer, at 5 nm intervals from 380 to 780 nm (ASTM E 308-99)**

**CIE L\*a\*b\* color parameters** [Gilchrist and Nobbs, 1999; El-Nagar et al., 2002; ASTM E308-99: 2001)

The a-axis runs from green to red, the b-axis runs from yellow to blue and L-axis (lightness) runs from black to white. As the Lab-diagram is a three dimensional diagram, the color difference between two points can be obtained in all directions.

The quantities of L, a and b are obtained from the tristimulus values according to the following transformation:

$$L = 116 \cdot (Y/Y_n)^{1/3} - 16 \quad \text{-----(5)}$$

$$a = 500 [(X/X_n)^{1/3} - (Y/Y_n)^{1/3}] \quad \text{-----(6)}$$

$$b = 200 [(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}] \quad \text{-----(7)}$$

where  $X_n$ ,  $Y_n$  and  $Z_n$  are the value of the illuminant that was used for the calculation X, Y and Z of the sample

The color difference can be calculated as follow:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad \text{-----(8)}$$

$$\Delta L = L_{\text{trl}} - L_{\text{std}} \quad \text{-----(9)}$$

$$\Delta a = a_{\text{trl}} - a_{\text{std}}, \text{ and} \quad \text{-----(10)}$$

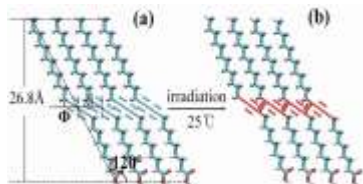
$$\Delta b = b_{\text{trl}} - b_{\text{std}} \quad \text{-----(11)}$$

- where the standard (std) L, or b is the value at the room temperature (25°C) and the measured (trl) at different temperatures.

#### Results and Discussion

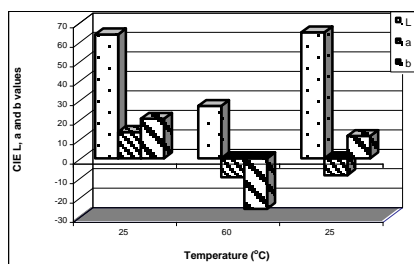
These PDA-Na microcrystals show interesting thermochromatic transitions at different temperatures. (Jiebin et al., 2006) equations (12-14) show color transitions of PDA-Na microcrystals (deposited on glass slides) at different temperatures. The microcrystals show a red color after topochemical 1,4-addition polymerization (Figure 2) of the diacetylenic units by exposure to room light at room temperature. The microcrystals undergo an irreversible color transition to blue (equation 12) when the crystals are heated to

ca. 65 °C, which remains upon cooling to room temperature. Interestingly, further heating of the blue crystals to a temperature of ca. 70-95 °C results in a completely reversible blue to red thermochromatic transition due to the enhanced electrostatic intermolecular interactions. The microcrystals maintain their reversible thermochromatic transition behavior even after multiple thermal cycles. However, heating the crystals to temperatures above 105 °C limits the degree of reversibility. Furthermore, if the sample is heated at a temperature higher than ca. 130 °C, a further irreversible chromatic transition to orange occurs. Such unique thermo chromatic transitions are of great interest for thermal sensors.

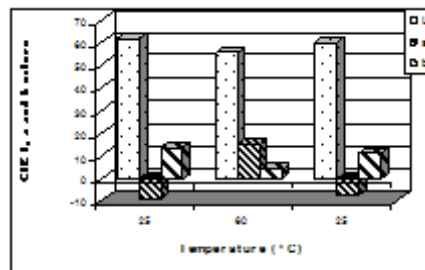


**Figure 2.** A schematic illustration of the topochemical polymerization of PCDA-Na molecules at room temperature: (a) before polymerization, (b) after polymerization. A  $d$  of about 5.06 Å is the monomer separation distance, and a  $\phi$  of about 43° is the angle between the diacetylenic unit and the stacking axis. A distance of 26.8 Å is the repeat length of one layer of diacetylene molecules before polymerization.

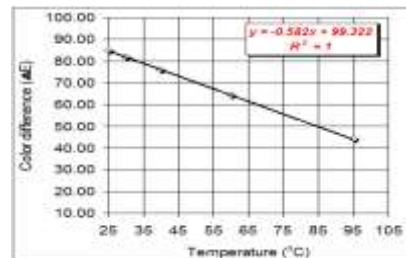
Figure (3) show that the starting polymer has a red color, which is resulted from the conjugated polydiacetylenic backbone that absorbs blue light. The red PDA-Na microcrystal possess monoclinic structure with unit cell parameters of  $a=5.29$  Å,  $b=9.80$  Å,  $c=57.37$  Å and  $\beta=120^\circ$  while the blue crystal possessed a similar monoclinic structure with unit cell parameters of  $a=5.10$  Å,  $b=9.79$  Å,  $c=55.56$  Å and  $\beta=95^\circ$ . Figure (4) represent the reversibility of color upon heating and cooling at temperature below 105°C and this attributed to the enhanced electrostatic interactions. XRD studies in the previous work demonstrated that no obvious change for the lamellar mesostructure during the reversible blue-to-red color transition (Jeibin et al., 2006; Jonas et al., 1999; Huang et al., 2005; Yuan et al., 2004). Figure 5 show the correlation between the temperature changes and the accompanied color variations. The regression factor was found equal unity which means the linear relation between the temperatures and the color difference. Also it gives the equation of correlation that by which we can detect the temperature as a function of the color difference. Figure (6) shows the effect of temperature of the PDA-Na film treated at a temperature higher than 130 and also indicates the irreversibility of the color. These variations also enable us to use PDA-NA as a disposal sensor for the temperature up to more than 130°C.



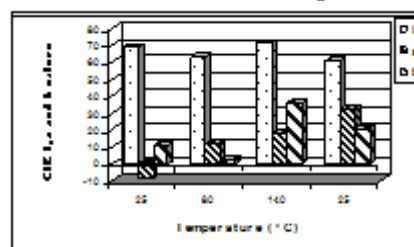
**Figure 3:** Effect of heat on the PCDA-Na (treated at <55°C) on the CIE color parameters L, a and b. Irreversible change (Pink-Blue-Blue)



**Figure 4:** Effect of heat on the PCDA-Na (treated at 65°C) on the CIE color parameters L, a and b. Reversible (Blue -Red -Blue)



**Figure 5:** Color difference ( $\Delta E$ ) - temperature correlation



**Figure 6:** Effect of heat on the PCDA-Na (treated at >130°C) on the CIE color parameters L, a and b. Irreversible (Blue-Red-Orange-Orange)

The highly unsaturated conjugated backbone of PPA imparts unusual physical properties including relatively large third order optical non linearity. This type of dichromic behavior is attributed to a change of effective conjugated length effect (Lio et al., 1997). Optical absorption in PDA occurs via  $\pi$ - $\pi^*$  absorption within linear  $\pi$ -conjugated polymer backbone. In general, PDA chromatic transition involves significant shift in absorption from low to high energy bonds of the visible spectrum; thus the PDA appears to transform from a blue to red color. The mechanism driving these transitions is not understood in details; it is believed that molecular conformational changes such as side chain packing, ordering, and orientation impart stresses to the polymer backbone that alter its conformation. The color change from blue to red arises from reduction of the effective conjugated length of the polymer ene-yne backbone. In the red phase of PDA the chains assure a rear-perfect hexagonal packing and films are thicker with respect to the blue form.

### Conclusions

The prepared polymer has an excellent thermo-chromatic response from deep blue to red. This response can be tuned easily by the variation of the surface's optical properties. Optical reflection behavior was converted into CIE color parameters L (lighting), a (red-green) and b (yellow blue). The resulted polymer after treated to 65 it turns to irreversible blue colored film. This blue colored film has recyclable response to the heat stimulation and this recyclability stands to all thermal changes from 25°C to 105°C and reverse. This recyclability enable us using this polymer structure as smart materials for the temperature changes in the range 25-105°C. Polymer (PDA-Na)

that is encapsulated in the polyacrylate films and applied to cellulosic fabric gives it the smart and sensing behavior towards the temperature changes and enables us to use it in different fields e.g. medical, fire fighting, and metrological application as a heat sensors.

#### Acknowledgment

Corresponding author thanks Prof. Ahmed Monir at the National Institute for Standards for his help and guidance.

#### References

Ahn, D. J., E. H. Chae, G.S. Lee, H.Y. Shim, T.E. Chang, K.D. Ahn, J.M. Kim, 2003. *J. Am. Chem. Soc.*, 125: 8976.  
American Standard testing Method (ASTM) number E308-99, Volume 6-01(2001)  
Angkaew, S., H. Y. Wang, J.B. Lando, 1994. *Chem. Mater.*, 6: 1444.  
El-Nagar Kh., A. Ramadan , E. Khalil, 2002. *Egypt J. of Appl. Sci.*, 17(8)(2002):100-111.  
El-Nagar Kh., S.H. Samaha, E.A EL-Alfy and F. M. Tera, *J. of Biophys.*, special issue, 1998:96-111.  
Gilchrist A. and J. Nobbs, 1999. *Colour by numbers . JSDC*, volume 115 January 1999 : 4-7  
Hang,X.; Jiang,S.G.; Liu,M.H.J.*Phys.Chem. B*2005,109,114].  
Hunt, R. W. G. (1999) *Measuring Colour*. (2nd edn) Tolworth, UK: Fountain Press  
Jiebin, P., L. Yang, F. B. McCaughey, H. Peng, S. Henry, C. Ashbaugh, J. Brinker, Y. Lu, 2006. *J. Phys. Chem. B* 110: 7221-7225]

Jonas, U., K. Shah, S. Norvez,D. H. Charych, 1999. *J. Am. Chem. Soc.* 121: 4580.  
Lio, A, A. Reichert, D.J. Ahn, J.O. Wagy, M. Solneron, D.H. Charych, 1997. *Langmuir*, 13:6524  
Lu, Y. F., Y. Yang, A. Sellinger, M.C. Lu, J. M. Huang, H. Y. Fan, R. Haddad, G. Lopez, A. R. Burns, D. Y. Sasaki, J. Shelnutt, C.J. Brinker, 2001. *Nature*, 410: 913.  
Mino, N., H. Tamura, K. Ogawa, 1991. *Langmuir*, 7: 2336.  
Okada, S., S. Peng, W. Spevak, D. Charych, 1998. *Acc. Chem. Res.* 31: 229  
Pires, A, N. Soares, L. Silva, N. Andrade, M. Silverira, A. deCarvalho, 2008. *Food Bioprocess Technology*.  
Tachibana, H., R. Kumai, N. Hosaka, Y. Tokura, 2001. *Chem. Mater.* 13:155.  
Yang, Y., Y.F. Lu, M. C. Lu, J. M. Huang, R. Haddad, G. Xomeritakis, N.G. Liu, A.P. Malanoski, D. Sturmayer, H. Y. Fan, D. Y. Sasaki, R.A. Assink, J. Shelnutt, F. van Swol, G. P. Lopez, A. R. Burns, C.J. Brinker, 2003. *J. Am. Chem. Soc.* 125:1269.  
Yuan, Z. Z., C.W. Lee, S. H. Lee, 2004. *Angew. Chem. Int. Ed.*, 43:4197  
Xiaoming Tao, 2001, *Smart Fibres, Fabrics and clothing*, 1st Ed., Woodhead publishing limited, UK: 2-3.