

# ZnO:Polydiacetylene Films as Chromic Sensors

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## ABSTRACT

Films of the conjugated polydiacetylenes (PDAs) can function as chromatic temperature, chemical and stress sensors, and can be prepared by spin-coating from monomer solutions followed by polymerization using UV- or  $\gamma$ - irradiation. PDAs thus have the potential for advanced applications as sensors

Nanocomposite ZnO:PDA and ZnO/ZrO<sub>2</sub>:PDA thin films have been prepared and their structural properties have been characterized by a variety of techniques including Fourier transform infrared spectroscopy, Raman spectroscopy, differential thermal calorimetry (DSC) and extended x-ray absorption fine structure (EXAFS) measurements. We have conducted testing and calibration of the thermal and stress sensing properties of the composite films using optical density measurements. It was also observed that the fluorescent red phase transforms to a non-flourescent blue phase in the presence of trace amounts of chemical vapors. Results on the sensing of trace amounts of vapors of tri-nitrotoluene (TNT) and dinitrotoluene (DNT) by optical densitometry and fluorescence, and efforts to enhance the chemical sensitivity of TNT detection by addition of single wall carbon nanotubes to the polydiacetylene (PDA), will also be discussed.

**Keywords:** polydiacetylenes, sensors, chromic, Army, thermal

## 1 INTRODUCTION

Materials that change color in response to external stimuli are of great interest to the U.S. Army. Chromic materials refer to those materials which radiate, lose color, or change properties induced by external stimuli. Different stimuli result in different responses in the material being affected. "Chromic" is a suffix that means color, so chromic materials are named based on the stimuli energy affecting them, for example:

photochromic - light

thermochromic – heat  
piezochromic – pressure  
solvatechromic – liquid  
electrochromic – electricity/voltage conflicts

Polydiacetylenes (PDAs) are a series of conjugated polymers which can undergo thermochromic transitions when exposed to stimuli. This chromic change is caused by the shortening of the conjugation length of the polymeric backbone [1]. Furthermore, the thermochromic transition temperature is a function of the side groups on the polymeric backbone structures. By changing the side groups, repeatable response to set stimuli are possible. This allows these materials to function as sensors. There are several applications of these PDAs as chromic sensors for Army applications.

The U.S. Army ARDEC is interested in chromic materials for sensing applications. As part of the Active Coatings Technologies Program, a research team was established to investigate chromic materials for active sensor systems and develop active/smart paints and coatings.

Films of these conjugated polydiacetylenes (PDAs) can function as chromatic temperature, chemical, and stress sensors, and are of particular interest to the Army.

## 2 TECHNICAL DISCUSSION

### 2.1 Materials Development

The conjugated PDA films are prepared by spin-coating monomer solutions followed by polymerization using UV- or  $\gamma$ - irradiation. The polymer backbone of PDAs is comprised of alternating double bonded (ene)-triple bonded (yne) groups which are responsible for intriguing temperature, stress and chemically-induced chromatic (blue, non-flourescent to red, fluorescent) transitions. Figure 1 illustrates basics of thermochromism in PDAs.

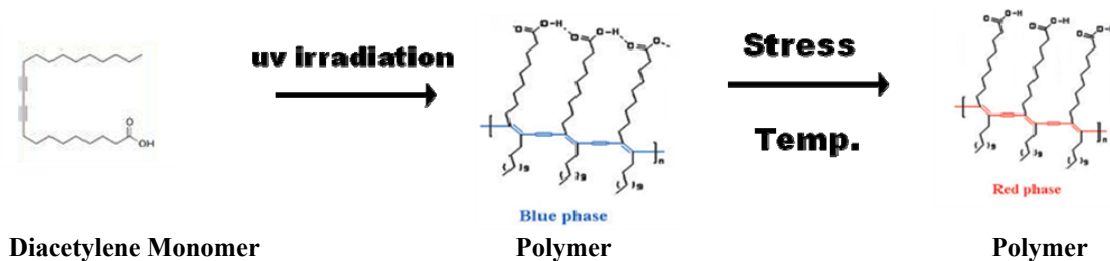


Figure 1. Illustration of monomer to polymer transition and Blue to Red Phase transition of PDAs.

Research on the properties of PDAs in the past has primarily focused on their large non-linear optical response originating from their long conjugated backbones [2]. More recently interest has shifted to the chromatic transitions exhibited by the PDAs [3]. The PDA monomers polymerize rapidly under external stimuli, such as uv-irradiation, and some of the polymers undergo chromatic phase transitions due to changes in the backbone structure and conformation [4]. The monomers are normally colorless and become increasingly blue with polymerization. Color in PDAs is a result of  $\pi$  to  $\pi^*$  electronic transitions associated with the  $C\equiv C-C\equiv C$  diacetylene backbone. Irreversible blue to red chromatic transitions occur in many PDAs under external stimuli. This also means that these PDAs will undergo phase changes in two stable states, the low temperature blue state and the high temperature red state.

Although these thermochromic polydiacetylene possess the desired properties of interest to the U.S. Army, in order for them to be acceptable solutions for military applications, the overall cost must be acceptable versus the added utility they will provide. If the PDAs and resulting films, coatings, paints, etc. are too expensive, difficult to apply, or causes other additional cost/time burdens, the Army will not implement them. Therefore, cost effective monomer and polymers to develop these PDAs were analyzed, tested, and selected.

The Army research team has found that ZnO uniquely forms a weak complex with acidic diacetylenes containing carboxylic groups: 10, 12-pentacosadiynoic acid (PCDA), 10, 12-docosadiynedioic acid (DCDA), and 10, 12-tricosadiynoic acid (TCDA), resulting in reversal of the chromatic blue to red transition. They have also observed that this reversibility is slowed down by mixing the PDA with an alloy of ZnO with  $ZrO_2$ , thus allowing the mixed oxide-PDA films to function as elapsed time-temperature indicators.

Three commercially available thermochromic PDA monomers were used as the active component in paint formulations developed for the Army. The PDA monomers selected have the following chemical structures:

- $CH_3(CH_2)_{11}-C\equiv C-C\equiv C-(CH_2)_8-COOH$   
(10,12 pentacosadiynoic acid-PCDA)
- $CH_3(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_8-COOH$   
(10,12 tricosadiynoic acid-TCDA)

- $HOOC-(CH_2)_8-C\equiv C-C\equiv C-(CH_2)_8-COOH$   
(10,12 docosadiynedioic acid -Bis-1)

PCDA and TCDA were found to show a blue to red transition with brighter contrast in the polymer phase compared with Bis-1. PCDA and TCDA were therefore incorporated in most of the formulations used. Bis-1 was added to either PCDA or TCDA in the higher temperature formulations to fine-tune the transition temperature.

The team discovered that nanosized Zinc oxide (ZnO) or a heat treated oxide alloy of ZnO and zirconium oxide ( $ZrO_2$ ) could be mixed into this formulation to control the reversibility of the chromatic transition.

## 2.2 Understanding effects of ZnO on Polydiacetylenes

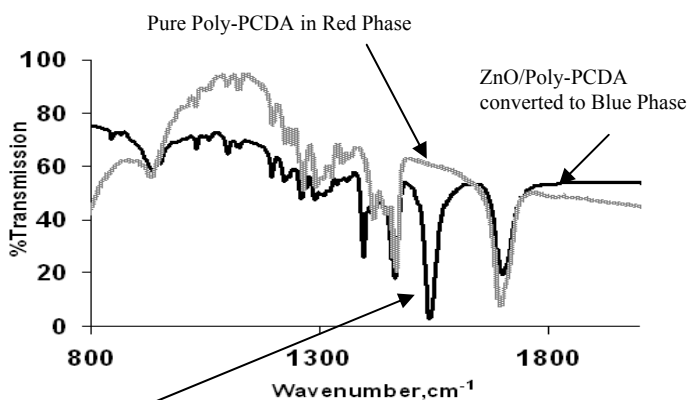
Nanocomposite ZnO:PDA and ZnO/ $ZrO_2$ :PDA thin films were prepared and their structural properties were characterized by a variety of techniques including FTIR, Raman spectroscopy, DSC and EXAFS measurements. FTIR was used to understand the role that pure ZnO has in affecting PDA thermochromisms. Figure 2 illustrates the effect.

Preliminary EXAFS results on poly-PDCA metal oxide nanocomposites show changes in the mean square disorder in Zn-Zn distances in the ZnO-poly-PCDA complex relative to pure ZnO (Figure 3). This is consistent with the bonding interactions between ZnO and poly-PCDA and supports the results indicated by the FTIR spectra.

Raman spectroscopy is another method used to characterize and understand the effects of ZnO,  $ZrO_2$ , ZnO/ $ZrO_2$  added to the PDAs being used. Figure 4 shows Raman Spectra of both the pure and mixed oxides of interest. A peak at  $425\text{ cm}^{-1}$  of the ZnO in mixed ZnO/ $ZrO_2$  shows a loss of intensity caused by the alloying. PDAs head group interactions with mixed oxides are different than those of pure ZnO, helping to understand the effects the oxides have and how to tailor the response of the materials to different stimuli.

Figure 5 and Figure 6 show the  $C\equiv C$  effect on the PDA backbone induced by addition of ZnO acting with the  $-COOH$  of the head groups (see at  $\sim 2260\text{ cm}^{-1}$  in Figure 6). Pure  $ZrO_2$  does not affect the irreversibility of the chromatic transition, but thermally alloying  $ZrO_2$  with ZnO was found to substantially slow down the rate of conversion of the red to the blue phase. Initial x-ray studies indicated

no change in crystal structure of ZnO on thermal treatment with  $ZrO_2$ .



Infrared line @  $1540\text{ cm}^{-1}$  in presence on ZnO is assigned to backbone C=C mode activated by ZnO interaction with head groups

Figure 2. FTIR showing role of ZnO in PDA chromism.

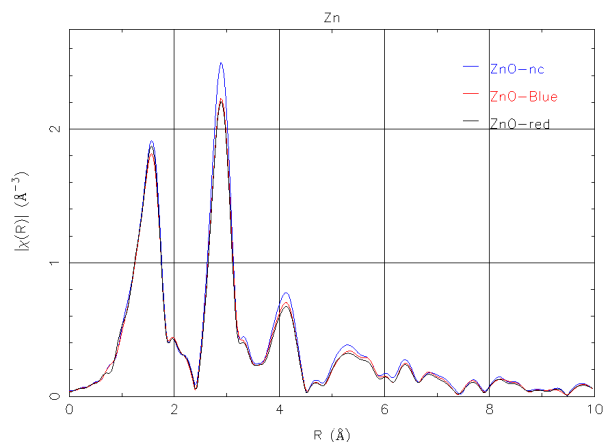


Figure 3. EXAFS spectra results of ZnO showing plots of ZnO nanocrystal (nc), Red Phase & Blue Phase.

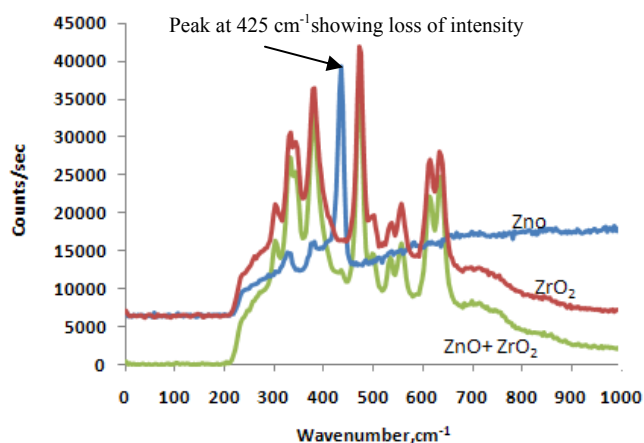


Figure 4. Raman Spectra of pure and mixed oxides.

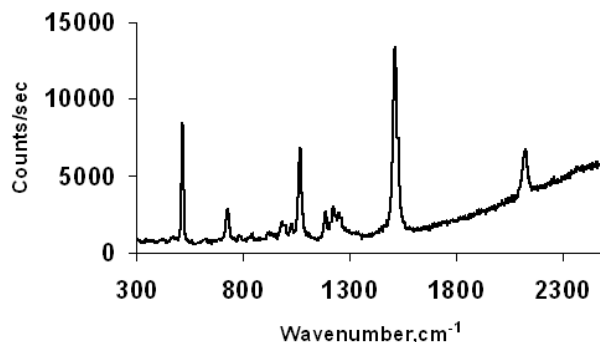


Figure 5. Pure Poly-PCDA in Red Phase (Raman 785 nm excitation).

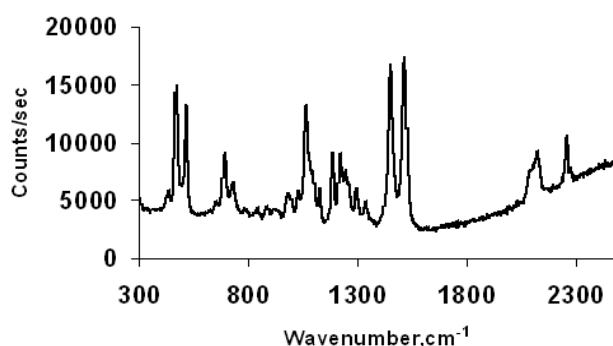


Figure 6. ZnO-poly PCDA in Red Phase converted to Blue Phase (Raman 785 nm excitation).

Both reversible and irreversible systems are possible. ZnO interactions can also take place with the head groups to repair hydrogen bonds and thus re-form the Blue Phase. Furthermore, reversing of the Red Phase to Blue Phase can be slowed down by using a mixed oxide of zinc and zirconium,  $ZnO/ZrO_2$ , in compositions near  $Zr_{1-x}Zn_xO_y$  where  $x=0.4$ . This interaction is believed to lead to the reversibility of the red phase and sizeable increase of the chromatic transition temperature in the poly-PCDA-ZnO nanocomposites. By understanding the effects of ZnO and  $ZrO_2$  and their interactions with the head groups of PDAs, the research team is able to control the reversibility and irreversibility of the chromic materials being developed.

### 2.3 Chromaticity of ZnO- and $ZrO_2$ Containing Polydiacetylene Nanocomposites for Sensing

The effect of ZnO and  $ZrO_2$  on PDA and the resulting measurable chromaticity of nanocomposite ZnO:PDA has led to the development ZnO:PDA films as chromatic sensors. By adjusting the formulations these materials can be modified to respond to thermal stimuli at a desired "trigger" temperature. The ability allows for thermal indicating paints, coatings, and films to serve as sensors for thermal exposure monitoring, as well as other applications.

While the “trigger” temperature will provide an easy “go/no go” indication of an item’s exposure to thermal conditions, the “soak” time or duration of exposure is important as well. As mentioned above, the addition of nanosized ZnO in pure form and alloyed with ZrO<sub>2</sub> can cause the red phase to revert to the blue phase at variable rates. Therefore paint formulations with added ZnO and mixtures of ZnO with ZrO<sub>2</sub> can be used to monitor the cumulative time of exposure in certain temperature ranges by measuring the chromaticity of the material. An optical densitometer can be used to accurately measure the resulting chromaticity. Chromaticity is a quantitative measure of the vividness or dullness of a color.

This provides both accurate visual cumulative time information as well as quantitative cumulative time information allowing ZnO:PDA to function as thermal indicating paints, coatings, films for thermochromic sensing applications.

Cumulative time of exposure in multiple temperature ranges can be sensed and optically detected by mixing small amounts of the time-temperature sensitive diacetylene monomers, and ZnO:PDA into the coating matrices. This allows for the thermal indicating paints, coatings, sensors, etc. to “remember” prior day exposures and monitor thermal cumulative thermal dwell or soak times.

Thermal indicating paints are being investigated by the Army for munitions monitoring, bake-off testing, and other applications where soldiers’ safety can be increased by providing early warning indicators of potential thermal exposures and off-gassing conditions.

It was also observed that fluorescent Red Phase transforms to a non-fluorescent Blue Phase in the presence of trace amounts of certain chemical vapors. There have been successful results on the sensing of these trace amounts of vapors, including tri-nitrotoluene (TNT) and dinitrotoluene (DNT), by optical densitometry and fluorescence.

TNT, DNT, and related stimulants (toluene) expresses the ability to open up the hydrogen bonds of the Blue Phase head groups and causing a predictable and controlled Red Phase transition. An effort to enhance the chemical sensitivity of TNT detection by infiltrating blue PCDA into high surface area microporous zeolite and addition of single wall carbon nanotubes is underway (Figure 7).

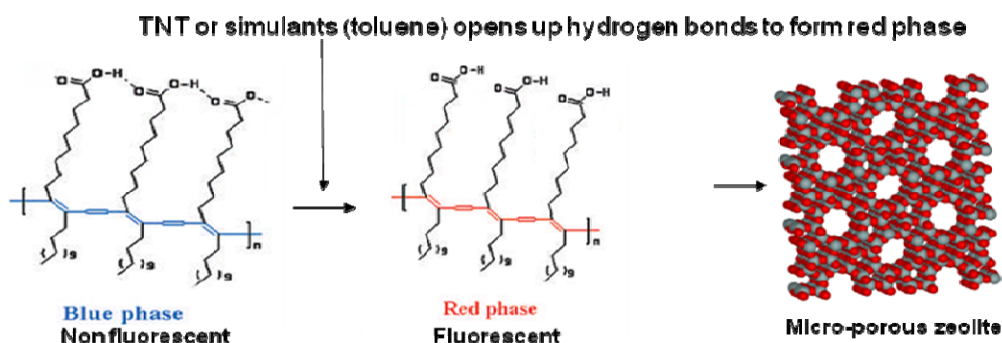


Figure 7. Opening of Blue Phase head groups by TNT or toluene will cause the Red Phase transition in zeolite at low concentrations.

This may allow stand-off detection for soldiers, first responders, etc. of IEDs and other potential dangers.

## 5. CONCLUSIONS

Polydiacetylene polymers that undergo chromic transitions when exposed to stimuli have great potential for cost effective sensing applications. Since the chromic transition is a function of the modification of head groups on the polymeric backbone structures, by changing these groups, repeatable response to set stimuli are possible. Understanding the effects of ZnO and ZrO<sub>2</sub> interactions with the head groups allows control of reversibility, irreversibility, and “triggered” response to desired stimuli.

This allows for the development of cost effective active or smart coatings, paints, films, etc. that can be utilized as sensors, indicators and warnings. The research being performed will directly and indirectly support the warfighter.

## 6. ACKNOWLEDGEMENTS

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