

## Studies of the blue to red phase transition in polydiacetylene nanocomposites and blends

Anitha Patlolla<sup>1</sup>, Qi Wang<sup>2</sup>, Anatoly Frenkel<sup>2</sup>, James L. Zunino III<sup>3</sup>, Donald R. Skelton<sup>3</sup> and

Zafar Iqbal<sup>1\*</sup>

<sup>1</sup>Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ 07102

<sup>2</sup>Department of Physics, Yeshiva University, New York, NY 10033 and Brookhaven National Laboratory, Upton, NY 11973

<sup>3</sup>U.S. Army ARDEC, Picatinny Arsenal, NJ 07806

### ABSTRACT

The conjugated polymeric backbone of polydiacetylenes (PDAs), comprising of alternating ene-yne groups, undergo intriguing stress-, chemical- or temperature-induced chromatic phase transitions associated with the disruption of the backbone structure and shortening of the conjugation length. PDAs, such as polymerized 10, 12 pentacosadiynoic acids (PCDA), when incorporated with inorganic oxides form nanocomposites and uniform blends with polymers. Blends of poly-PCDA with polymers, such as polyvinyl alcohol, polyvinylidene fluoride and cellulose increase the blue to red transition temperature without affecting the irreversibility of the red phase. However, the addition of zinc oxide to pure poly-PCDA makes the red phase highly reversible and substantially increases the blue to red transition temperature. The addition of TiO<sub>2</sub> to poly-PCDA on the other hand does not affect the irreversibility of the red phase and the chromatic transition temperature. In order to understand the atomic scale interactions associated with these changes in the chromatic transitions, we have investigated both the nanocomposites and polymer blends using Raman and Fourier-transform infrared spectroscopy, and extended X-ray absorption fine structure (EXAFS) measurements.

### Introduction

Polydiacetylenes (PDAs) are a unique class of conjugated polymers which undergo dramatic thermochromic and chemically-induced chromatic transitions [1] due to shortening of the conjugation length of the polymeric backbone [2]. Modification of the polydiacetylenes as nanocomposites integrated into inorganic host matrices can have significant effects on their chromatic transitions [3]. It was also reported that the thermochromic transition temperatures are a function of the nature of the side groups on the polymer backbone and the structure of the substituents [4]. A number of the polydiacetylenes in the form of nanocomposites have been synthesized and their chromatic responses to various stimuli have been demonstrated.

Previous studies of the mechanism of the solid state phase transitions in the polydiacetylenes [5] have demonstrated that structural changes occur independently in the polydiacetylene backbone and hydrocarbon side chains of PDAs to give rise to the chromatic transitions. It was also reported that changes do not occur directly in the distribution of electron density along the backbone when chromatic effects are induced [6], but side chain interactions

lead to strain on the diacetylene backbone [7] to give rise to the chromatic transformations. Many of the thermochromic transitions are irreversible with decrease of temperature, but chemically-induced chromatic transitions which enhance multiple hydrogen bonding, strong aromatic or ionic interactions between head groups or some level of covalent bonding, can be reversed by removing the adsorbed molecules to recover the original length of the conjugated  $\pi$  electron backbone [8].

In this work, near-resonance Raman and Fourier transform infrared (FTIR) spectroscopy together with EXAFS (Extended X-ray Absorption Fine Structure) measurements have been used to study PDA-polymer and PDA-metal oxide interactions, and the possible nature of the chromatic phase transitions in these materials. The PDA used in the present study is poly (10, 12-pentacosadynoic acid).

## EXPERIMENTAL DETAILS

Zinc oxide, titanium dioxide, cellulose, and polyvinyl alcohol (PVA) were purchased from Sigma-Aldrich, PCDA (10, 12-pentacosadiynoic acid) was purchased from GFS Chemicals, and polyvinylidene fluoride (PVDF) was purchased from Polysciences Inc. The average molecular weights of PVA are 30,000-70,000 from low angle light scattering and of PVDF is 80,000. The polydispersity values for PVDF and PVA are:  $\sim 2.5$ - $3.0$  and  $\sim 1.9$ , respectively. These parameters are not available for cellulose.

1:1 ratio by weight poly-PCDA - metal oxide composites investigated in this study were prepared by mixing solutions and suspensions in chloroform of PCDA and the oxides of titanium and zinc. The solids obtained were UV irradiated at 254 nm for 5 minutes to form the polymeric poly-PCDA blue phase and heated above the transition temperature to form the red phase. 1:1 ratio by weight polymer blends of poly-PCDA with PVA, PVDF and cellulose were similarly prepared and converted to the blue and red phases. Thin films from the solutions or suspensions were prepared by dip-coating on silicon wafers at room temperature. The chromatic transition temperatures were measured on thin films prepared by spin coating using an aliquot of 2 mM of PCDA in chloroform on microscope glass slides at the rate of 2000 rpm. Spin coating films of different metal oxide suspensions containing 1:1 weight ratio of PCDA and metal oxide and polymer suspensions, was performed at the same rate on glass slides.

Powders of poly-PCDA-metal oxide composites in the blue and red phases were used for the EXAFS measurements. Raman measurements were performed both on thin films and powders of the nanocomposites and polymer blends. Samples for FTIR spectroscopy were prepared by pressing KBr pellets of the nanocomposites and polymer blends in a die.

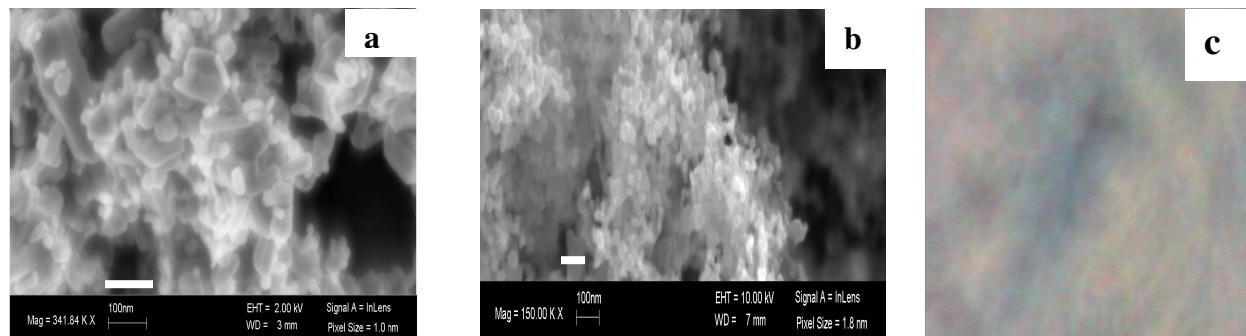
FTIR spectra were obtained using a Perkin Elmer FTIR spectrometer. The Raman spectra were obtained using a Mesophotonics Raman spectrometer with 785 nm laser excitation. EXAFS measurements were carried out using the Synchrotron Light Source at the Brookhaven National Laboratory. SEM and optical images were obtained with a LEO scanning electron microscope and a Ken-A-Vision optical imaging microscope.

## RESULTS AND DISCUSSION

Scanning electron microscope (SEM) images of zinc oxide and titanium dioxide powders are shown in Fig. 1 (a) and Fig. 1 (b), respectively. A relatively wide distribution of sizes above and below 100 nm is seen for zinc oxide, whereas titanium dioxide shows a more uniform distribution of particle sizes around 100 nm. An optical image of a poly-PCDA: PVDF blend

shown in Fig. 1(c) indicates a fairly uniform mixing of the two polymers at a spatial resolution of around 2  $\mu\text{m}$ .

The chromatic blue to red phase transitions are of three types: reversible, partially reversible, and irreversible, which have been explained in terms of hydrogen bonding interactions.



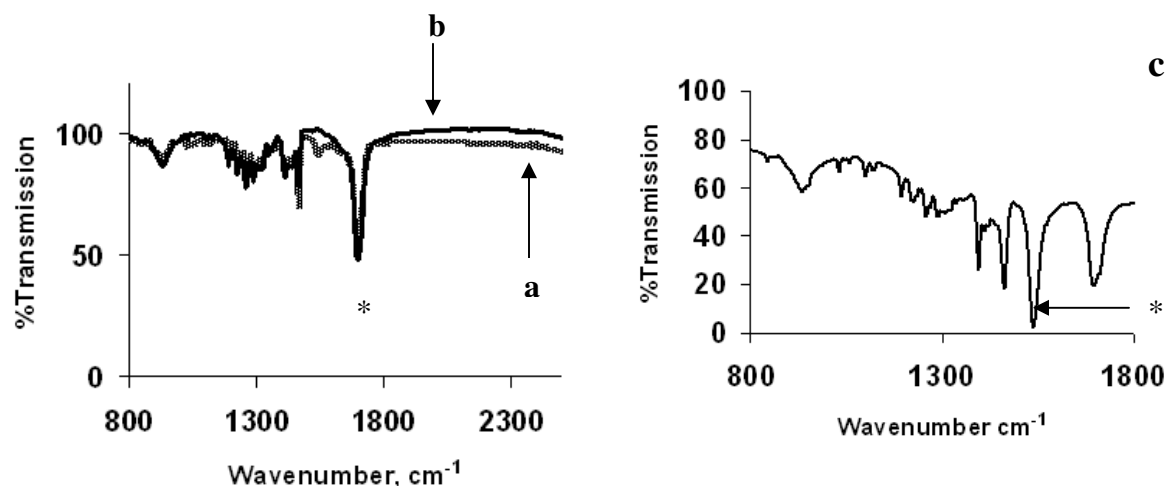
**FIGURE 1.** (a) and (b) Scanning electron microscope (SEM) images with scale bar shown below the images of pure zinc oxide powder and pure titanium dioxide powder, respectively; and (c) Optical microscope image of 1:1 weight ratio of polydiacetylene (poly-PCDA): PVDF taken with a 40x objective at a spatial resolution of approximately 2  $\mu\text{m}$ .

Complete thermochromic reversibility from the red to the blue phase takes place in PDAs where sufficiently strong hydrogen bonding interactions remain unchanged throughout the thermal cycle [9]. Interactions of this type involving double hydrogen bonding among the head groups can also be induced by the addition of specific organic molecules. It was therefore surprising that the addition of the inorganic compound ZnO to the PDAs induced chromatic reversibility and a large upshift of the chromatic transition temperature. By contrast, the addition of  $\text{TiO}_2$  and  $\text{ZrO}_2$  did not affect the chromatic transition parameters.

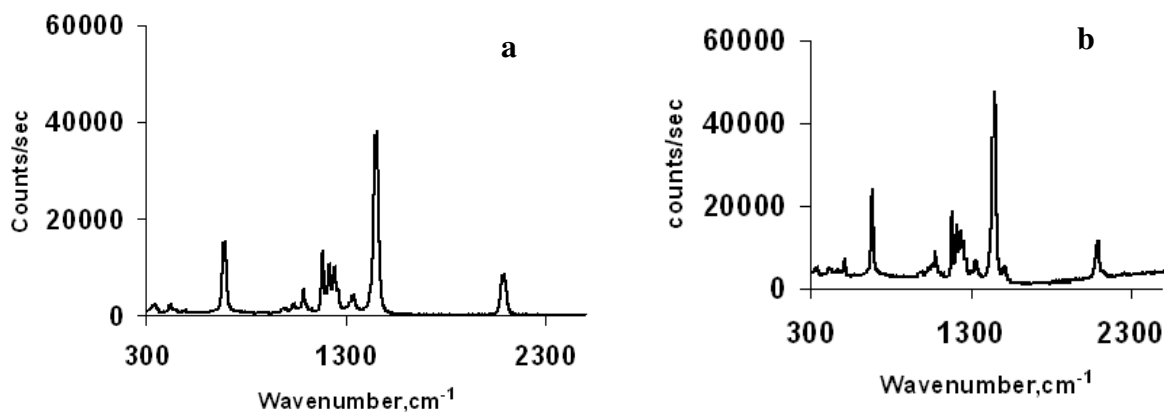
The FTIR spectrum for the poly-PCDA-ZnO nanocomposite in Fig. 2c shows a large increase in intensity of the line at  $1540\text{ cm}^{-1}$ . This line is relatively weak in the FTIR spectrum of pure poly-PCDA (Fig. 2a) and is not observed in the spectrum of the nanocomposite of poly-PCDA with  $\text{TiO}_2$  (Fig. 2b). The  $1540\text{ cm}^{-1}$  line is also observed with relatively high intensity in the FTIR spectrum of the red phase of the poly-PCDA-ZnO nanocomposite (not shown). However, by contrast to the FTIR spectrum in Fig. 2c for the blue phase of the poly-PCDA-ZnO nanocomposite, there is a substantial decrease in intensity of the C=O stretching line at  $1688\text{ cm}^{-1}$  in the red phase. This suggests an interaction between ZnO and the -COOH head group of the PDA side chain, resulting in infrared activation of the line at  $1540\text{ cm}^{-1}$ , which is close to the Raman frequency at  $1515\text{ cm}^{-1}$  of the C=C stretching mode in the red phase (Fig. 4b). The line at  $1540\text{ cm}^{-1}$  can therefore be assigned to an infrared-activated C=C stretching mode in the poly-PCDA-ZnO nanocomposite. The corresponding C=C stretching resonance-enhanced Raman line in the blue phase is at  $1451\text{ cm}^{-1}$  (Fig.3) due to increased conjugation. The infrared activated C=C mode frequency is the same in both the blue and red phases because, unlike the resonance Raman spectra, the conjugation length of the polymer backbone does not influence the infrared spectra. A new Raman line in the C $\equiv$ C region at  $2258\text{ cm}^{-1}$  appears in the red phase but not in blue phase (Fig. 4). Further studies are needed to understand the activation mechanism for this line, which probably also results from changes in the PDA backbone due to the interaction of ZnO with the -COOH group on the side-chain. Other lines appearing in the Raman spectra of the

red phase of the poly-PCDA-ZnO nanocomposite in Fig. 4b are due to the emergence of the blue phase in the presence of ZnO. The thermochromic transition of the blue to the red phase in the poly-PCDA-ZnO nanocomposite results in an upshift of the resonantly enhanced C=C stretching Raman frequency from  $1449\text{ cm}^{-1}$  to  $1515\text{ cm}^{-1}$  and of the C≡C stretching Raman frequency from  $2089\text{ cm}^{-1}$  to  $2122\text{ cm}^{-1}$  (Fig. 4) due to decrease in conjugation length of the PDA backbone.

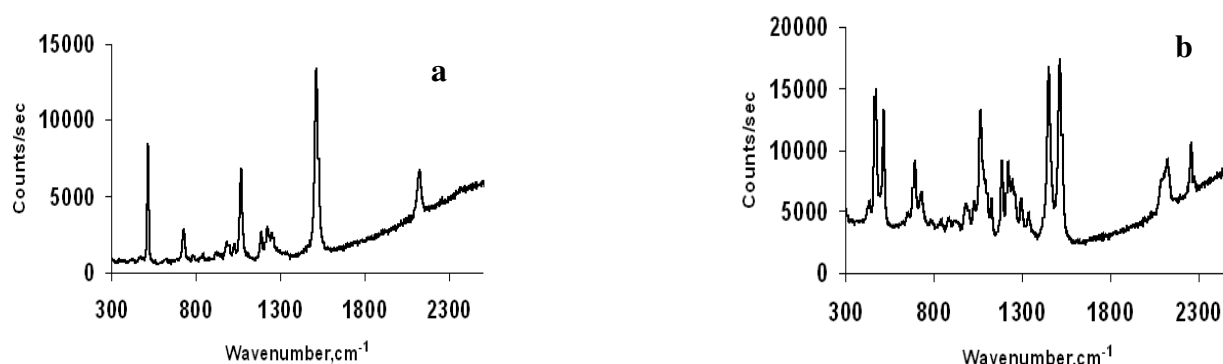
The FTIR spectra of poly-PCDA show small differences relative to the pure diacetylene on addition of PVA, PVDF and cellulose, indicating weak interactions between the polymers in these blends. This is consistent with up shifts observed in the transition temperatures of the blends relative to that of the pure polydiacetylene. Preliminary EXAFS studies on poly-PCDA metal oxide nanocomposites show changes in the mean square disorder in Zn-Zn distances in the ZnO-poly-PCDA complex relative to pure ZnO (Fig. 5a), consistent with the bonding interactions between ZnO and poly-PCDA indicated by the FTIR spectra. Similar differences in the EXAFS data are not observed in the poly-PCDA-TiO<sub>2</sub> nanocomposite relative to the data for pure TiO<sub>2</sub> (Fig. 5b).



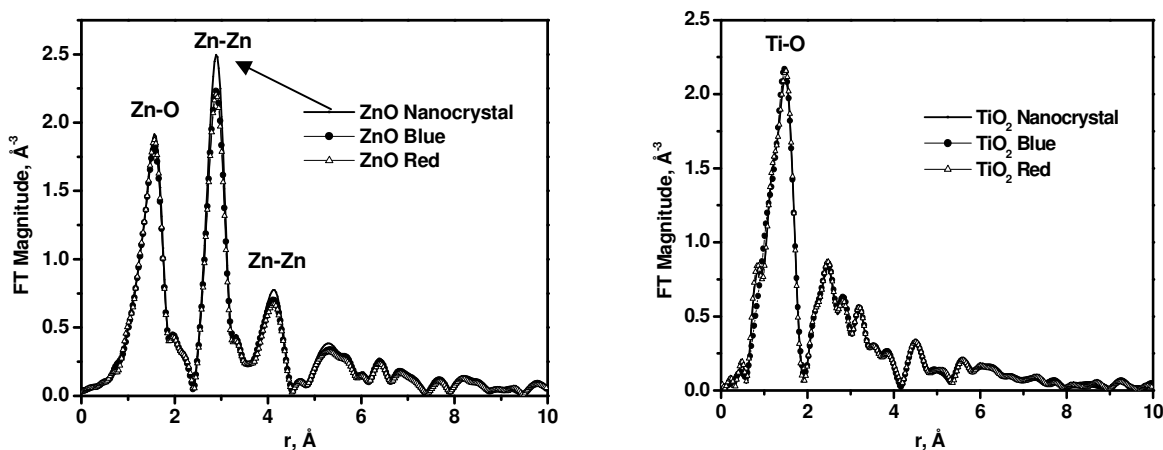
**FIGURE 2.** FTIR spectra of poly-PCDA in the blue phase mixed as composites with metal oxides: Spectrum a) Pure poly-PCDA, b) Poly-PCDA: titanium dioxide (1:1 weight %) nanocomposite, and c) Poly-PCDA: zinc oxide (1:1 weight %) nanocomposite. The line at  $1540\text{ cm}^{-1}$  discussed in the text is indicated by an asterisk.



**FIGURE 3.** Near-resonance Raman spectra in the 300 to 2300  $\text{cm}^{-1}$  region of: a) Pure poly-PCDA in the blue phase, and b) 1:1 weight % nanocomposite of poly-PCDA with zinc oxide in the blue phase. The spectra were taken with the powder spread uniformly on a silicon wafer.



**FIGURE 4:** Near-resonance Raman spectra in the 300 to 2300  $\text{cm}^{-1}$  region of: (a) Poly-PCDA in the red phase, and (b) 1:1 weight % nanocomposite of poly-PCDA nanocomposite with zinc oxide in the red phase partially converted to the blue phase.



(a) (b)  
**FIGURE 5.** EXAFS spectra shown as plots of the Fourier transform magnitude of EXAFS oscillations in  $r$ -space for: (a) ZnO and ZnO composites with poly-PCDA in the blue and red phases; and (b)  $\text{TiO}_2$  and  $\text{TiO}_2$  composites with poly-PCDA in the blue and red phases.

## CONCLUSIONS

FTIR, Raman and EXAFS data for poly-PCDA nanocomposites with zinc oxide and titanium dioxide indicate bonding interactions only with zinc oxide involving the head group of the diacetylene side chain. This interaction results in the infrared activation of a  $\text{C}=\text{C}$  bond stretching mode at  $1540 \text{ cm}^{-1}$ , a sizeable decrease in intensity of the  $\text{C}=\text{O}$  stretching line in the FTIR spectrum, and the appearance of a new  $\text{C}\equiv\text{C}$  Raman line at  $2259 \text{ cm}^{-1}$  in the red phase of the poly-PCDA-ZnO nanocomposite. This interaction probably leads to the reversibility of the red phase and sizeable increase of the chromatic transition temperature in the poly-PCDA-ZnO

nanocomposite. Weak interactions between poly-PCDA blended with PVDF, cellulose and PVA, are also indicated by shifts of the Raman and FTIR spectra and increase in the blue to red transition temperatures, but these interactions are not strong enough to promote reversibility of the red phase in poly-PCDA blends with these polymers.

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\*Corresponding author: iqbal@adm.njit.edu

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