

Micropatterning of Polydiacetylene Based on a Photoinduced Chromatic Transition and Mechanism Study

Wenfang Yuan,^{1,2} Guiyuan Jiang,³ Yanlin Song,¹ Lei Jiang¹

¹Organic Solids Laboratory, Institute of Chemistry and Center for Molecular Science, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

²Graduate School, Chinese Academy of Sciences, People's Republic of China

³State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, People's Republic of China

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ABSTRACT: A photoinduced chromatic transition from blue to red for the polydiacetylene 10,12-pentacosadiynoic acid has been studied. This transition produces an obvious change in the ultraviolet-visible absorption and fluorescence emission spectra. A two-dimensional micropattern has been realized on the basis of this change and imaged with a confocal fluorescence microscope. Detailed information on the mechanism of the chromatic transition has been obtained by the application of resonance Raman and

Fourier transform infrared methods. The results indicate that the conformational change of alkyl side chains constricted by hydrogen-bonded head groups imposes strain on the polymer backbone and finally leads to a drastic decrease in the π -electron-conjugation length. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 942–946, 2007

Key words: conjugated polymers; fluorescence; photophysics; solid-state polymerization; stimuli-sensitive polymers

INTRODUCTION

Polydiacetylenes (PDAs), a class of highly π -conjugated polymers, are considered attractive candidates for the development of many optical¹ and electrical devices because of their unique properties, such as a quasi-one-dimensional electronic structure, a high third-order nonlinear optical response, and very fast photoconduction properties.^{2–5}

In past decades, research on the optical properties of PDAs has been mainly focused on their large nonlinear response, which originates from the long conjugated backbones,⁶ but another interesting property, that is, the photoinduced chromatic transition of PDAs, has been less recognized. PDAs can undergo phase changes in two stable states, the blue state and the red state, in response to external stimuli, such as heat,⁷ solvents,⁸ and light.^{9,10} This property

has attracted much attention recently, especially in biochemistry. However, applications of this property to optical devices have been rarely reported. Because the photoinduced chromatic change meets the basic requirement of information storage, we are exploring PDA applications in optical devices, especially optical data storage. To this end, two-dimensional optical data storage in solid films of a typical PDA molecule, 10,12-pentacosadiynoic acid (PCDA), is demonstrated in this article; the blue and red states before and after the photoinduced transition represent the 0 and 1 states of the data storage, respectively, and the stored data are read out via the fluorescence contrast between the two states. To understand the underlying principle of the transition, resonance Raman (RR) and Fourier transform infrared (FTIR) have been conducted. Unlike previous researchers, who believed that the transition was caused by side-chain movement from an ordered state to a less ordered state,¹¹ we have found that the photochromic transition is accompanied by an alkyl-side-chain movement to a more ordered state that is constrained by the hydrogen bonds between the head groups and finally leads to a reduced conjugated length in the polymer backbones. This system can be suggested as an alternative approach for read-only-memory systems, and our study may be helpful for the exploration of other optical applications of PDAs.

Correspondence to: Y. Song (ylsong@iccas.ac.cn).

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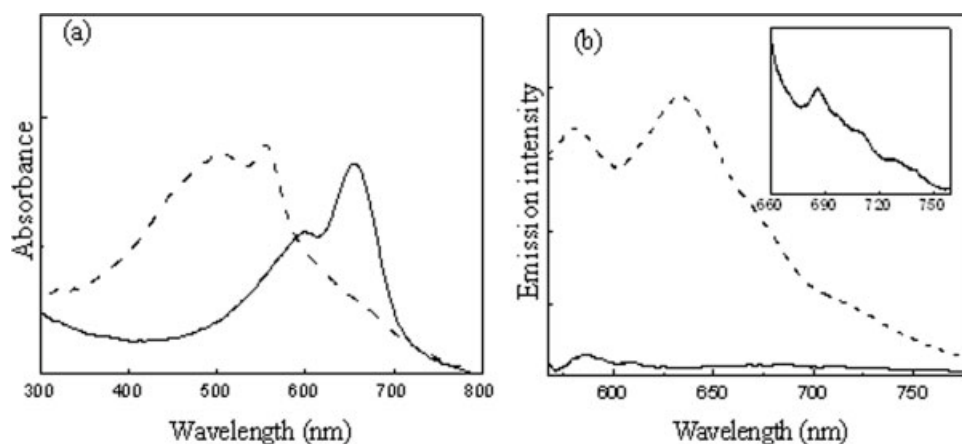


Figure 1 (a) UV-vis absorption spectra and (b) fluorescence emission spectra of PDA films excited at 532 nm. The solid line represents the blue polymer formed by UV irradiation for 2 min, and the dashed line represents the red polymer formed by UV irradiation for 30 min. The inset is the fluorescence spectrum of the blue polymer excited at 650 nm.

EXPERIMENTAL

Materials

PCDA [$\text{CH}_3-(\text{CH}_2)_{11}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_8-\text{COOH}$; Aldrich Steinheim, Switzerland] was employed as a diacetylene compound¹²⁻¹⁴ and used as received. Dichloromethane was an analytical reagent and was used without further purification.

Preparation of the PCDA films and two-dimensional patterning

The diacetylene monomer was dissolved in a solvent of dichloromethane with a concentration of 1 mg/mL. The solution was coated onto different substrates for different optical measurements, namely, quartz for ultraviolet-visible (UV-vis) absorption and fluorescence, KBr for FTIR, and glass for RR and confocal microscopy. The films were dried thoroughly in the dark at room temperature. The polymerization and photoinduced chromatic transition were performed by UV irradiation with a high-pressure mercury lamp through a UV-transmitting filter with a power of 7 mW/cm². All the experiments were conducted in the dark except for the polymerized samples. For two-dimensional patterning, first, a film with a thickness of about 20 μm was totally exposed to UV-light irradiation for 2 min to polymerize, and then it was irradiated through a dot-patterned contact photomask with features in the micrometer-size regime for about 30 min. After irradiation, the photomask was removed, and the image was successfully transferred to the polymer film.

Measurements

A Hitachi (Tokyo, Japan) U-4100 UV-vis spectrophotometer and a Hitachi (Tokyo, Japan) F-4500 fluorescence spectrophotometer were used for the measure-

ment of the UV-vis absorption spectra and fluorescence emission spectra, respectively. For the fluorescence imaging of the two-dimensional micropattern, the confocal mode of a Witec-Alpha scanning near-field optical microscope (Ulm, Germany) with 532-nm excitation was used. The photoluminescence was separated from the excitation light by a color-glass, long-pass filter (OG 570, Schott Mainz, Germany).

FTIR spectra before and after light irradiation were measured with a Nicolet Magna IR 750 spectrometer (Nicolet Analytical Instruments Madison, WI). The Renishaw RM2000 microscopic confocal Raman spectrometer (Gloucestershire, United Kingdom) was used for RR measurements with a microscope objective lens (20 \times). The focused laser spot size was about 5 μm . The Raman spectra were acquired with 632.8-nm laser excitation, and the laser power at the sample spot was 47 μW .

RESULTS AND DISCUSSION

Figure 1(a) presents the change in the absorption spectra of a polymerized PCDA film in the photoinduced chromatic transition. Monomer films of PCDA are very sensitive to the irradiation of UV light, turning blue because of photopolymerization. Further UV irradiation causes a chromatic conversion from blue to red. In the initial stage of the process, an absorbance band with peaks at 600 and 655 nm emerges. The peak at 655 nm (exciton band) corresponds to the $\pi-\pi^*$ electronic transition to the first allowed excited state. The weaker band at 600 nm (vibronic band) results from the coupling of the main transition to the stretching modes of the backbone.¹⁵ After prolonged UV irradiation, the absorption band of the red form appears, with an absorbance maximum at 554 nm for the exciton band and at 502 nm

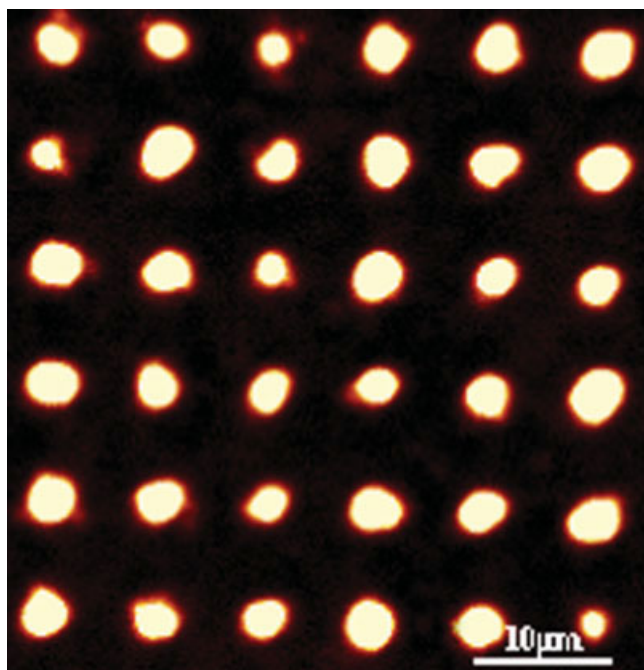


Figure 2 Fluorescence image of a two-dimensional micropattern formed in a polymerized PCDA film. The light regions are luminescent, and the dark regions are nonluminescent with an excitation wavelength of 532 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for the vibronic band.¹⁵ The blueshift of the absorption bands for these two forms indicates the reduction of the effective delocalization length of the π electron; that is, the red form has a shorter delocalization length of the π electron than the blue form.¹⁶ In the photostationary state of the chromatic transition, the absorption at 655 nm does not disappear completely.

Corresponding to the difference between the UV-vis absorption before and after the phase transition, the luminescence response of PCDA is also dictated by the binary states. Figure 1(b) presents the fluorescence emission spectra of these two forms excited at 532 nm, and the inset figure presents the blue form excited at 650 nm. The blue polymer shows a very weak fluorescence emission, whereas the red polymer has a strong emission band excited at 532 nm with a maximum occurring at 580 and 633 nm. The contrasting variance of the fluorescence emission intensity of these two forms can be explored to read data for optical information storage.

To demonstrate the photoresponsive property, two-dimensional micropatterns were created in polymerized PCDA films through UV irradiation by the selective protection of the prepolymerized films, which were in the blue form, with a dot-patterned photomask. As stated previously, there is a contrasting variance of the fluorescence emission intensity of these two forms. Thus, it is possible to read out the

formed patterns on the basis of this difference. In the case of this experiment, a confocal fluorescence microscope was used. Figure 2 illustrates a representative image generated by these experiments. The masked areas that are still in the blue form appear dark, and those unmasked areas that undergo a chromatic transition appear luminescent. The selective chromatic transition demonstrated in our experiments, with the resultant luminescence activation and deactivation, indicates the potential application of PDA to optical recording.¹⁷

To further understand the underlying principles of the photoinduced chromatic transition, RR and FTIR spectra before and after the transition were measured. The Raman spectra are shown in Figure 3. For the blue form, there exist two major bands at 2079 and 1451 cm^{-1} , which are assigned to the stretching modes of the triple and double carbon-carbon bands in the polymer backbone, respectively.¹⁸ For the red form, four major bands at 2119, 2079, 1514, and 1451 cm^{-1} appear, of which the two at 2079 and 1451 cm^{-1} are identical to those of the blue form. The new ones at 2119 and 1514 cm^{-1} can be attributed to the triple and double carbon-carbon stretching modes of the red form, and the shifts to a high wave number can be ascribed to the change in the bond structure in the conjugated polymer backbone.¹⁸ In combination with the UV-vis absorption spectra, in which the red form still has absorption at 600–700 nm, it can be concluded that the small peaks at 2079 and 1451 cm^{-1} belong to a small residue of blue forms. Similar results have been reported for a thermochromic PDA TCDU.¹⁹

Figure 4 shows the FTIR spectra of PCDA in its blue and red forms. The former shows strong absorption bands at 2920 and 2848 cm^{-1} , which can be attributed to asymmetric ν_{as} (CH_2) and symmetric ν_{s} (CH_2) stretching vibrations, respectively.²⁰ With

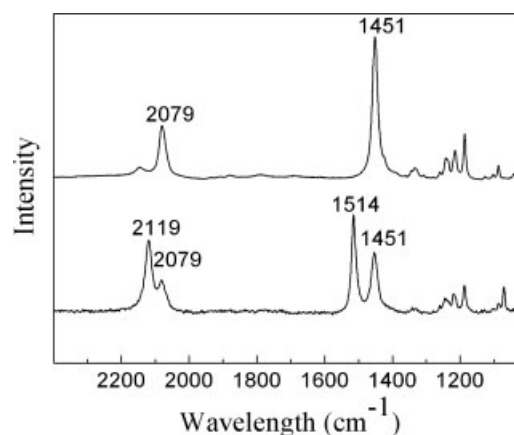


Figure 3 Raman spectra of the blue and red forms of PDA with 632.8-nm excitation. The upper spectrum represents the blue form, and the lower spectrum represents the red form.

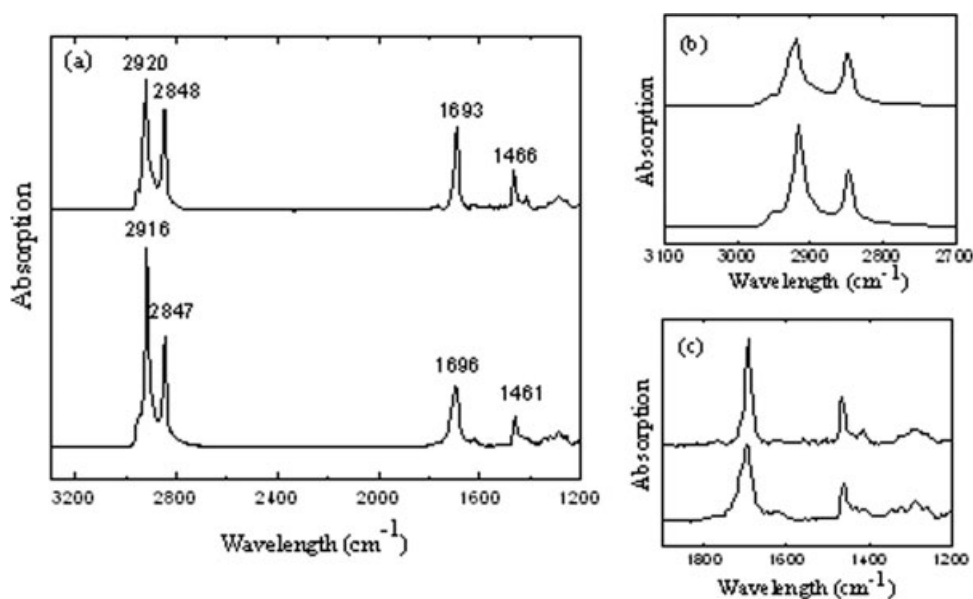


Figure 4 (a) FTIR spectra of the blue and red forms of PCDA and (b,c) corresponding high-resolution spectra. The upper spectra represent the blue form, and the lower spectra represent the red form.

respect to the blue form, the $\nu_{\text{as}}(\text{CH}_2)$ peak of the red form shifts to a lower wave number by 4 cm^{-1} , whereas the $\nu_{\text{s}}(\text{CH}_2)$ peak changes little. The peak at 1693 cm^{-1} of the blue form can be assigned to the carbonyl band [$\nu(\text{C}=\text{O})$] of strongly hydrogen-bonded carboxylic acid head groups.^{21,22} For the red form, the carbonyl stretching band appears at 1696 cm^{-1} , shifts to a higher wavelength by 3 cm^{-1} , and slightly broadens, indicating that hydrogen bonding in the head group is maintained, though somewhat reduced. Also observable in the FTIR spectra is the scissoring band of the methylene group, which is at 1466 cm^{-1} and shifts to 1461 cm^{-1} after 30 min of UV irradiation. The band progression at $1350\text{--}1200\text{ cm}^{-1}$ due to the CH_2 wagging vibrations is observable in both spectra.

It has been reported that the photoinduced color transition from blue to red is caused by a side-chain movement from an ordered state to a less ordered state, which leads to the conformational change of the PDA backbones from planar to nonplanar and finally the reduced effective conjugated length of the ene-yne polymer backbone.¹⁴ In our case, a decrease in the π -electron-conjugation length has been confirmed by UV-vis absorption and Raman spectra. However, in IR spectra, a low frequency shift of 4 cm^{-1} of $\nu_{\text{as}}(\text{CH}_2)$ of the alkyl side chains can be observed. As is known, the $\nu_{\text{as}}(\text{CH}_2)$ vibration is conformation-sensitive, and a shift to lower frequencies for the $\nu_{\text{as}}(\text{CH}_2)$ vibration indicates more ordered conformations.²³ Thus, it can be concluded that during the blue-to-red transformation, the side chains undergo a transition to a more ordered state. At the same time, the hydrogen-bonding interaction

of carboxylic acid is still maintained and may lock the head groups. Thus, the conformational change of the side chains constrained by the locked head groups would cause more strain on the polymer backbone.^{24,25} Studies have suggested that the strains imposed on the backbone may result in a nonplanar backbone conformation produced by a slight rotation around the single bond, which finally causes a drastic decrease in the π -electron-conjugation length.²⁶

CONCLUSIONS

A photoinduced chromatic transition from the blue form to the red form of the PDA PCDA has been studied. A two-dimensional micropattern has been realized on the basis of this change and imaged by a confocal microscope employing the fluorescence difference between the two forms. The results of RR and FTIR indicate that hydrogen bonding of the head groups and conformational changes of the pendant alkyl side chains play important roles in the photoinduced chromatic transition. It can be proposed that the change of the alkyl chains to a more ordered state constricted by hydrogen bonding imposes strain on the polymer backbone, which finally leads to a drastic decrease in the π -electron-conjugation length. This study may throw new light on the mechanism study and application research of the photoinduced chromatic transition of PDAs.

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