

UV-Induced Chromatism of Polydiacetylenic Assemblies

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Highly ordered lamellar polydiacetylene nanocomposites are synthesized by assembling polydiacetylene and azobenzene through a ready solution process. The trans-to-cis transition of azobenzene under UV light induces a conformational change of polydiacetylene with a color change from blue to red.

Introduction

The chromatic transition between blue and red observed in polydiacetylene (PDA, in forms of vesicles or films) has been widely explored as a platform for the development of optoelectronic devices and biosensors.^{1–3} The blue-to-red chromatism is due to the decrease of effective conjugation length in PDA induced by the order–disorder transition of side chains under external stimuli including temperature,^{4–6} ions,⁷ solvent,⁸ pH/salt change,⁹ mechanical stress,¹⁰ or specific interaction between surface-bound ligand and complementary target.¹¹ Recently, great efforts have been also made to explore PDA with new sensing functionalities such as current-induced chromatism,¹² but to the best of our knowledge, few PDA systems with light-induced color changes have been reported to date.¹³ On the other hand, light-induced chromatic behavior in PDA can be advantageous for many environmentally benign photofunctional systems, e.g., photonics, optical storage, and photoswitchable materials.¹⁴

Azobenzene derivatives are well-known as photoactive systems with unique conformation changes, e.g., trans to cis under UV irradiation.¹⁵ During the trans-to-cis transition, azobenzene moieties become shorter and may pull on neighboring chains to induce their conformation changes.¹⁶ Therefore, if side chains of PDA are connected to azobenzene components, the above conformation changes in side chains will decrease the conjugation length of the PDA backbone with chromatic transitions. Based on this molecular design, we study nanocomposite materials assembled from 4,4'-azodianiline and a series of diacetylenic acids with different chain lengths between the diacetylenic bond and carboxyl (Figure 1). As widely explored, ionic interaction, π – π stacking, and hydrophobic and electrostatic interactions between acidic and basic pairs may organize building blocks into highly ordered lamellar structures.¹⁷ Subsequent polymerization of diacetylenic components produces PDA assemblies.^{18,19}

Experimental Section

Material. 5,7-Octadecadiynoic acid (97.4%), 6,8-nonadecadiynoic acid (96.7%), 8,10-heneicosadiynoic acid (95.0%), and 10,12-pentacosadiynoic acid (95.0%) were purchased from GFS

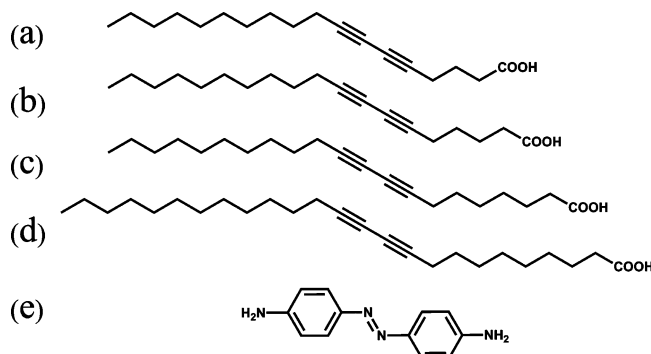


Figure 1. Molecular structures of (a) 5,7-octadecadiynoic acid, (b) 6,8-nonadecadiynoic acid, (c) 8,10-heneicosadiynoic acid, (d) 10,12-pentacosadiynoic acid, and (e) 4,4'-azodianiline.

Chemicals, Inc. 4,4'-Azodianiline (95%), *p*-xylylenediamine (97%), and tetrahydrofuran ($\geq 99.0\%$) were obtained from Acros Organics, Sigma-Aldrich, and Sinopharm Chemical Reagent Co., respectively. Chemicals were used as received unless specified.

Synthesis of Polydiacetylenic Nanocomposite Film. Diacetylenic acid and 4,4'-azodianiline were separately dissolved in THF with concentrations higher than 10 mg/mL (e.g., 15 mg/mL). After ultrasonic treatment of 10 min, the above solutions were filtered with nylon membrane (pore diameter of 0.22 μm , used to remove impurities and precipitants) and diluted to 10 mg/mL, respectively. 4,4'-Azodianiline solution was dropped into diacetylenic acid solution with a molar ratio of 1/1 between NH_2 and COOH groups under ultrasound. The mixture solutions were spin-coated onto glass slides (12 mm \times 12 mm) to fabricate films after evaporation of solvent at room temperature. Finally, PDA nanocomposite films were synthesized by topochemical polymerization of diacetylenic components under UV light (365 nm, 6 W) according to a previously reported procedure.^{18,19} UV light with a wavelength of 254 nm (6 W) was used to induce the chromatic transition of PDA films with a distance between the lamp and the sample of ~ 12 cm. All operations were carried out at room temperature.

Characterization. Morphologies were characterized by scanning electron microscopy (Hitachi FE-SEM S-4800) and transmission electron microscopy (JEOL 2010). Structure characterization was conducted using X-ray diffraction (XRD; Bruker D4 X-ray diffractometer, Ni-filtered $\text{Cu K}\alpha$ radiation at $\lambda = 0.15418$ nm, operated at 30 kV and 30 mA). UV–visible

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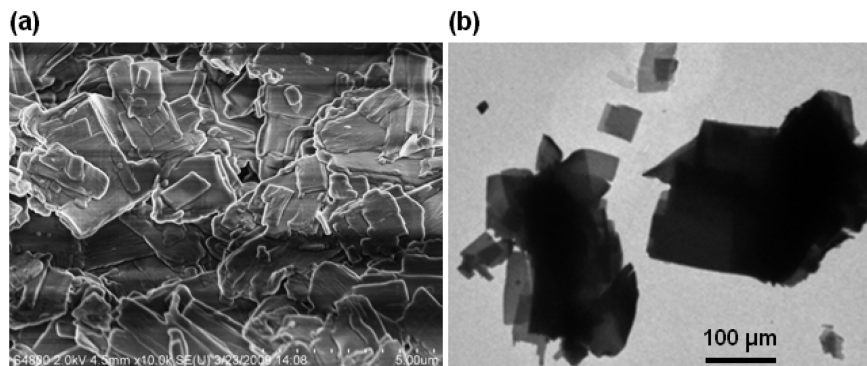


Figure 2. PDA nanocomposites derived from 4,4'-azodianiline and 5,7-octadecadiynoic acid. (a) Scanning electron microscopy image. (b) Transmission electron microscopy image.

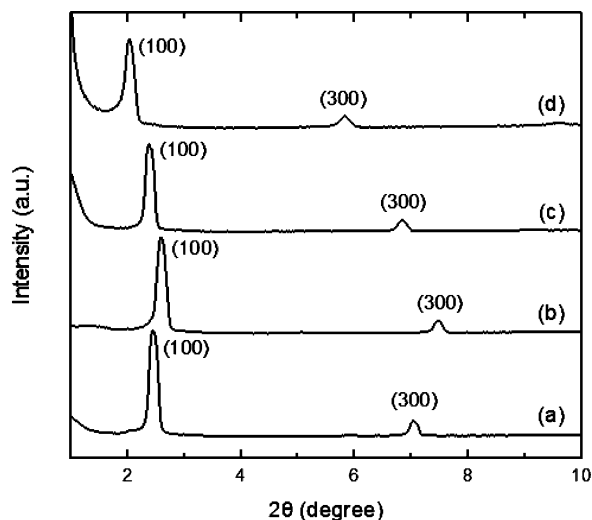


Figure 3. X-ray diffraction patterns of PDA nanocomposites derived from 4,4'-azodianiline and (a) 5,7-octadecadiynoic acid, (b) 6,8-nonadecadiynoic acid, (c) 8,10-heneicosadiynoic acid, and (d) 10,12-pentacosadiynoic acid.

spectra of composite films were recorded using a Shimadzu U-3150 spectrophotometer. Fourier transform infrared (FTIR) spectra were obtained on a Shimadzu IRPrestige-21 FTIR Spectrometer.

Results and Discussion

In a typical synthesis, 4,4'-azodianiline solution (10 mg/mL) was dropped into colorless diacetylenic acid (e.g., 5,7-octadecadiynoic acid) solution (10 mg/mL) with a molar ratio of 1/1 between NH_2 and COOH groups to form complexes. 5,7-Octadecadiynoic acid/4,4'-azodianiline films were then prepared by spin-coating the above mixture solution onto glass slides, followed by evaporation of solvent at room temperature. Finally, blue PDA nanocomposites were synthesized by polymerizing diacetylenic moieties of the above films.^{20,21} Complexation between diacetylenic acid and 4,4'-azodianiline was confirmed by FTIR spectroscopy; i.e., the COOH peak at 1690 cm^{-1} was replaced by an asymmetric COO^- stretch at 1622 cm^{-1} in nanocomposite films.^{22,23} Scanning electron microscopy and transmission electron microscopy images show that PDA nanocomposites are composed of crystalline-like plates (Figure 2). The plates vary in size from several to hundreds of micrometers. X-ray diffraction patterns further confirm highly ordered lamellar structures of PDA nanocomposites (Figure 3). The strong (100) peaks correspond to the d -spacing of 3.61, 3.42, 3.71, and 4.32 nm for PDA nanocomposites derived from

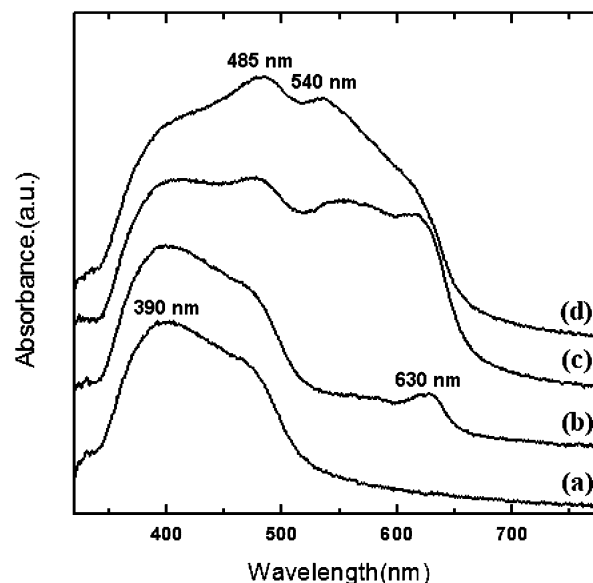


Figure 4. UV-vis spectra of (a) 4,4'-azodianiline/5,7-octadecadiynoic acid film and (b) derived blue PDA film, (c) exposure of (b) to UV light for 2.5 h, and (d) exposure of (b) to UV light for 12 h. The wavelength used of UV light is 254 nm.

5,7-octadecadiynoic acid, 6,8-nonadecadiynoic acid, 8,10-heneicosadiynoic acid, and 10,12-pentacosadiynoic acid, respectively. The interlamellar distances can be related to the lengths of building 4,4'-azodianiline and the related diacetylenic acid. It should be noted that the interlamellar distance of PDA nanocomposite synthesized from 6,8-nonadecadiynoic acid is smaller than that from 5,7-octadecadiynoic acid, possibly due to an odd-even effect of the carbon chain.²⁴

We investigated chromatic properties of PDA nanocomposites by a UV-vis spectrometer. Figure 4 indicates UV-vis spectra of 5,7-octadecadiynoic acid/4,4'-azodianiline and derived PDA films at different color stages. Absorption bands for trans and cis forms are located at ~ 390 and ~ 485 nm, respectively.²⁵ For 5,7-octadecadiynoic acid/4,4'-azodianiline films, the content of the trans form can be calculated to be $\sim 55\%$ from the peak intensities in Figure 4a, i.e., $A_{\text{trans}}/(A_{\text{trans}} + A_{\text{cis}}) \times 100\%$, where A is the peak intensity. After formation of blue PDA films, the trans isomer maintains the same 55% (Figure 4b), while a new peak characteristic of blue PDA appears at ~ 630 nm. As expected, UV irradiation (wavelength of 254 nm) decreases the peak intensity at ~ 390 nm and increases the peak intensity at ~ 485 nm (Figure 4c,d). The content of the trans isomer decreases to 45% and the content of the cis isomer increases to 55% after 12 h. During this process, the peak intensity at ~ 630

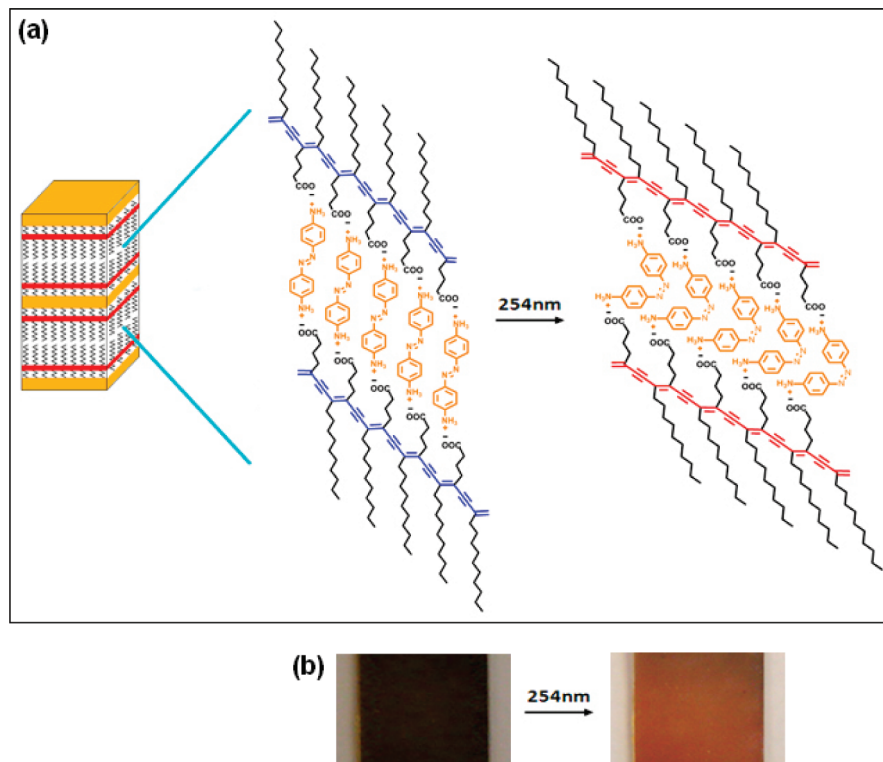


Figure 5. PDA nanocomposite films with ordered lamellar mesostructure derived from 4,4'-azodianiline and 5,7-octadecadiynoic acid. (a) Schematic illustration of trans-to-cis transition in azobenzene under UV irradiation and chromatism of complexed PDA. (b) Photographs of blue and red films during the above process.

nm first increases due to further polymerization of diacetylenic moieties and then quickly decreases; at the same time, a new peak at ~ 540 nm attributed to red PDA appears and its intensity gradually increases. It should be also noted that the d -spacing of PDA nanocomposite films changes, e.g., 3.45 nm for red PDA nanocomposites. As a comparison, we synthesized blue PDA nanocomposite films with a highly order lamellar mesostructure (Figure S1 in the Supporting Information) from *p*-xylylenediamine and 5,7-octadecadiynoic acid and irradiated them under the same conditions. The derived blue films maintained blue even after weeks (Figure S2 in the Supporting Information). In addition, no color changes have been observed for pure PDA, e.g., synthesized from 10,12-pentacosadiynoic acid, in days under the same UV setup. These results demonstrate that the trans-to-cis transition in azobenzene is responsive for UV-induced chromatism of PDA nanocomposites.

The above conclusion has been further confirmed by the fact that longer side chains in PDA largely decrease their chromatic efficiencies under UV light. Replacing 5,7-octadecadiynoic acid with 6,8-nonadecadiynoic acid with an increase of one CH_2 group between the diacetylenic bond and carboxyl, similar UV-induced chromatism was observed for the resulting PDA nanocomposite films. However, much less blue PDA becomes red compared to 5,7-octadecadiynoic acid (Figure S3 in the Supporting Information) under the same conditions. In the cases of 8,10-heneicosadiynoic acid (six CH_2 groups between the diacetylenic bond and carboxyl) and 10,12-pentacosadiynoic acid (eight CH_2 groups between the diacetylenic bond and carboxyl), derived blue PDA nanocomposite films maintained blue after days (Figure S4 in the Supporting Information). This phenomenon is reasonable considering that the trans-to-cis transition is transferred to the PDA backbone through side chains, and increasing the CH_2 groups in the side chains between the azobenzene unit and PDA decreases the transfer efficiency;

at critical CH_2 groups of six or higher, the transfer efficiency is too low to induce a conformation change of PDA.

Conclusions

In summary, we have synthesized highly ordered lamellar PDA nanocomposite films by assembling PDA and azobenzene through a ready solution process. The trans-to-cis transition of azobenzene under UV light may induce a conformation change of PDA with color changes through pulling on its side chains (Figure 5a). Lengths of the side chains play a critical role for the transfer efficiency of the conformation change from azobenzene to PDA. UV-induced chromatism from blue to red in PDA films can be safely, readily, and accurately performed, and this color change may be directly observed by the naked eye (Figure 5b). These advantages provide them numerous sensing applications. This research also affords an efficient molecular design and assembly paradigm to fabricate a family of sensing materials.

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Supporting Information Available: Figures S1 and S2 show X-ray diffraction pattern and UV-vis spectrum of PDA nanocomposite films prepared from 5,7-octadecadiynoic and *p*-xylylenediamine, respectively. Figure S3 shows UV-vis spectra of 4,4'-azodianiline/8,10-heneicosadiynoic acid film and derived PDA film. Figure S4 shows UV-vis spectra of 4,4'-azodianiline/10,12-pentacosadiynoic acid film and derived PDA

film. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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