

Chromatic polydiacetylene with novel sensitivity

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Conjugated polymers have been investigated for a number of applications in optoelectronics and sensing due to their important electronic and optical properties. For instance, polydiacetylene (PDA) may change color in response to external stimuli and has been extensively explored as a material for chromatic sensors. However, the practical applications of PDA materials have been largely hampered by their irreversible chromatic transitions under limited stimuli such as temperature, pH, and chemical. As a result, much effort has been paid to improve the chromatic reversibility and increase the scope of external stimuli for PDA. In this *tutorial review*, the recent development of PDA materials which show reversible chromatic transition and respond to new stimuli including light and electrical current has been described.

1. Introduction

Due to their excellent electronic and optical properties enabled by the extended π -electron delocalization along backbones, conjugated polymers have been widely investigated for a broad spectrum of promising applications, *e.g.*, sensing devices.¹ At this point, conjugated polymer-based sensors demonstrate an important advantage of amplifying signals in response to external stimuli compared to conventional sensors based on small molecules. Among them, polydiacetylene (PDA) represents one of the most explored conjugated polymers, and has shown some very useful structural and sensing properties.^{2–6} PDA can be easily synthesized by polymerizing diacetylenic monomers under ultraviolet or γ -irradiation at room temperature. As no catalysts or initiators have been added during the polymerization, the resulting PDA shows high purity which is important for sensing applications. In addition, PDA materials have been fabricated with tunable forms of aggregates, films, and powders through a neat

self-assembly process. Most important, as a sensing material, the typical color change from blue to red for PDA under external stimuli can be directly observed by the naked eye.

Since the first synthesis by Wegner in 1969,⁷ PDA has been widely studied and developed by several groups. For instance, Ringsdorf *et al.* prepared PDA membranes and vesicles in the 1970s and 1980s, respectively;^{8,9} Charych *et al.* firstly fabricated PDA materials for biosensing applications in the 1990s.¹⁰ In addition, a lot of studies including polymerization of diacetylenic monomers,¹¹ PDA vesicles,^{12–14} biosensing applications,^{15,16} and fluorogenic properties as well as new technological developments^{17,18} have been recently reported.

Although PDA has been widely proposed as an ideal candidate for sensing materials, its practical applications are largely limited by two big challenges. Firstly, the chromatic responses of most PDA materials are irreversible. For instance, when heated at high temperature, PDA easily changes color from blue to red, however, the red PDA may not return to the original blue as required for a good sensor after being cooled down to room temperature. Secondly, PDA responds to a limited range of environmental stimuli such as temperature, pH, chemical, stress, and ligand interaction. In order to solve the above two limitations, a lot of effort has been recently expended to design and fabricate novel PDA materials,

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particularly, the formation of nanocomposites with other organic or inorganic moieties which can greatly improve the chromatic properties of PDA.

This tutorial review highlights the recent development in the improvement of chromatic reversibility and chromatic transition in response to new stimuli in PDA nanocomposites. For the convenience of readers, the basic synthesis and characterization of PDA are first briefly summarized in this review. Then the emphasis is placed on the reversible chromatic transition of PDA under heating, pH, and two new stimuli of light and electric current.

2. Chromatic polydiacetylene

2.1 Synthesis of polydiacetylene

PDA materials have been synthesized through self-assembly of diacetylenic monomers (chemical structure of $R1-C\equiv C-C\equiv C-R2$), followed by 1,4-photopolymerization of diacetylenes under ambient conditions such as ultraviolet irradiation. R1 and R2 form the side chains of the resulting PDA. Fig. 1 shows the chemical structure of diacetylenic monomers with different side chains. The side chain can be composed of two main parts: a polar head group and a spacer between the head group and the diacetylene. The composition and structure of the side chains have been shown to be critical to the assembly structure and the polymerization of the

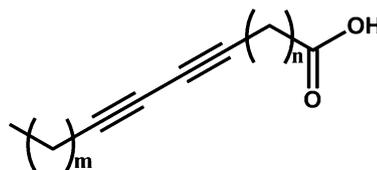


Fig. 1 The chemical structure of representative diacetylenic monomers with different side chains.

diacetylene. For instance, Evans and co-workers had demonstrated that odd and even numbers of methylene units as well as their lengths in the spacer greatly affected the assembly mesostructures.¹⁹ The diacetylenic monomers with even spacers were found to form more disordered PDA compared to those with odd spacers. It has been well explored that photopolymerization strongly depends on the arrangement order of the building diacetylenic monomers. Fig. 2 shows that diacetylenic moieties undergo polymerization only when they are highly packed with each other.¹¹ As a result, the odd-numbered methylene spacers lead to longer conjugation lengths after polymerization, while even-numbered spacers produced shorter conjugation lengths. In addition, the polymerization kinetics are significantly dependent on the methylene spacer length, *i.e.*, a longer chain favors faster polymerization.

2.2 Forms of polydiacetylene

PDA materials have been prepared mainly in three forms: films, aggregates in solutions (*e.g.*, vesicle), and powders. The formation of films and aggregates has been recently reviewed by Reppy *et al.*¹⁶ For instance, PDA Langmuir films are fabricated by assembling amphiphilic diacetylenic molecules at air/water interfaces, followed by photopolymerization; PDA vesicles are synthesized through self-assembly of diacetylenic amphiphiles in water. Recently, Kim *et al.* showed that further coating of the above vesicles on substrates produced novel PDA films composed of PDA vesicles.¹⁷ The PDA powders have been typically synthesized by a sol-gel process.²⁰ Diacetylenic monomers were used as surfactants and co-assembled with silsesquioxanes. The following hydrolysis and condensation reaction of silsesquioxane and photopolymerization of diacetylenic moieties produce PDA/silica nanocomposite powders. Diacetylene can also be directly



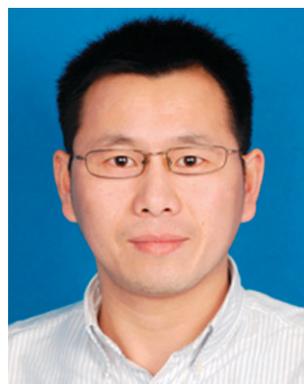
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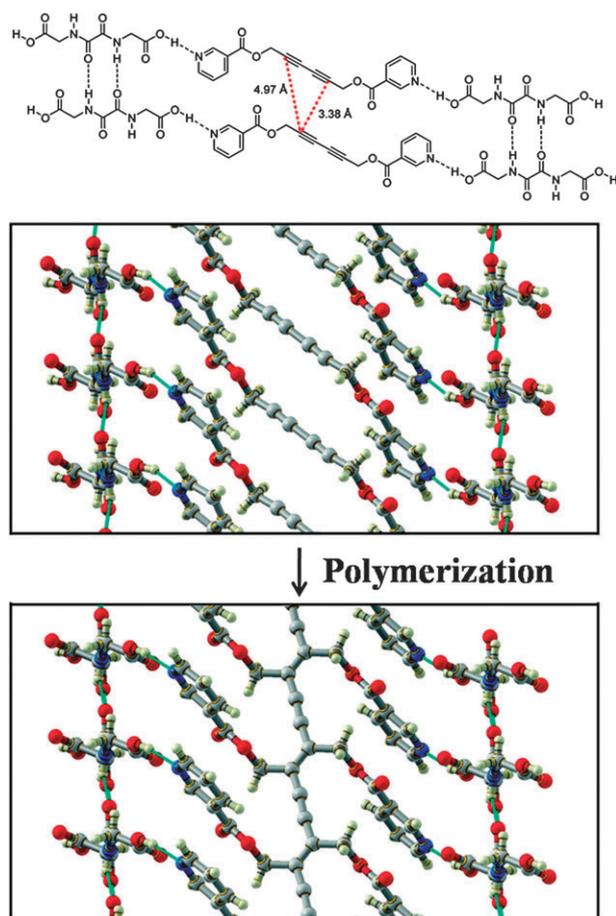


Fig. 2 A scheme showing that diacetylenic moieties undergo polymerization only when they are highly packed with each other. (Reproduced with permission from ref. 11. Copyright 2008, American Chemical Society.)

incorporated into silsesquioxanes to form PDA nanocomposite powders.

2.3 Chromatic characterization of polydiacetylene

Typically, diacetylenic monomers are colorless and the resulting PDAs appear blue after the photopolymerization. The blue PDA further turns red after exposure to specific external stimuli. It is widely accepted that this color change is produced by alternation of the PDA conformation under stimuli. More precisely, increased motional freedom of the PDA side chains caused by stimuli allows more disordered (and less coplanar) polymer with lower characteristic conjugation length.

The blue-to-red transition is mainly characterized by UV-vis spectroscopy. Fig. 3a shows the typical UV-vis spectra for a blue and red PDA film (induced by heating at high temperature). The peak associated with a blue phase appears at ~ 660 nm, while the peaks corresponding to the red phase occur at ~ 550 and ~ 500 nm. A peak at ~ 600 nm has been often observed in the spectra and attributed to an intermediate “purple” form between the red and the blue ones. However, it should be noted that this “purple” form is different from a real purple color derived from a mixture of blue and red forms.

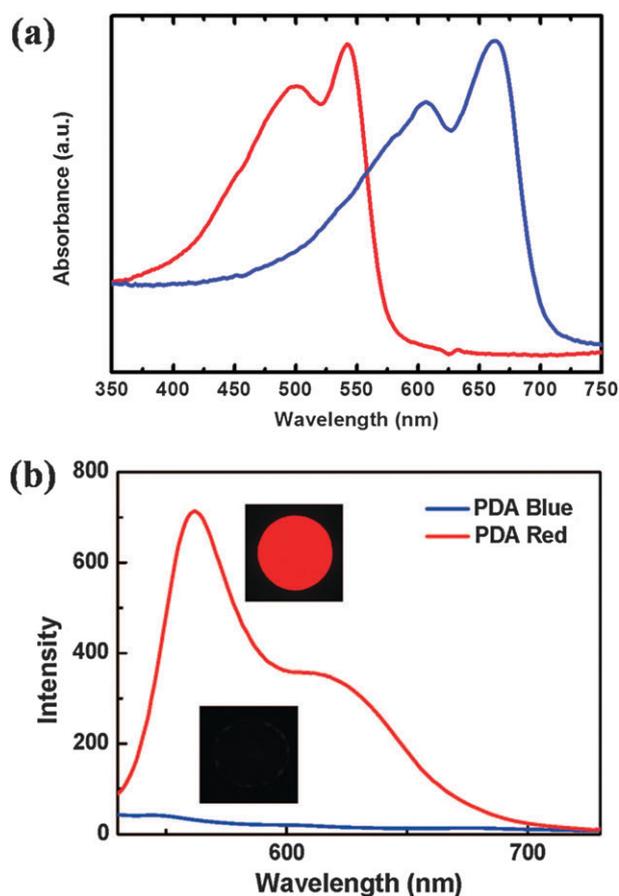


Fig. 3 The typical characterizations of blue and red phases of PDA. (a) UV-vis spectra. (b) Fluorescent spectra. (Reproduced with permission from ref. 17. Copyright 2008, American Chemical Society.)

Green and yellow PDA materials have also been synthesized with absorbance peaks at ~ 450 and ~ 440 nm, respectively. The above different colors and peaks in the PDA are dependent on the extent of polymerization, the structure of side chain, the form of material, and the exposure to environmental stimuli.¹⁶

Based on the UV-vis spectra, the chromatic response can also be quantitatively calculated by colorimetric response (CR), which is defined as the percentage from blue to red. Firstly, the initial (B_0) and final (B_f) blue percents are determined by $(A_{\text{blue}}/[A_{\text{blue}} + A_{\text{red}}]) \times 100\%$, where A is the peak intensity corresponding to the “blue” or “red” form. Then, $\text{CR} = (B_0 - B_f)/B_0 \times 100\%$. For a complete blue-to-red transition, B_f equals 0 and CR is therefore 100%.

The blue-to-red transition has also been efficiently characterized by fluorescent spectroscopy.²¹ The red PDAs are fluorescent due to the lowest excited B_u state, while the blue PDAs with A_g symmetry are non-fluorescent as the dipole transition can be forbidden during the emission from a singlet excited state.¹⁷ Therefore, the chromatic responses of PDA materials can be easily confirmed by tracing the appearance or disappearance of their fluorescent signals. Fig. 3b represents a typical fluorescent spectra for the blue and red phases of a PDA. Resonance Raman spectroscopy has been also often used to probe the change in ene-yne units of the backbone in PDA during a chromatic transition.

3. Polydiacetylene with reversible thermochromatism

Thermochromatism is one of the earliest reported chromatic properties of polydiacetylene.²² It has been shown that irreversible thermochromatisms resulted from irreversible structural transitions, while reversible thermochromatisms depended on reversible structural modifications.^{23,24} To improve the thermochromatic reversibility, PDA materials have been designed and fabricated by three main modifications in side chains, *i.e.*, introduction of other conjugated organic units such as azobenzene, enhancement of hydrogen-bonding interactions among the head groups, and incorporation of rigid and stable inorganic frameworks such as silica.

3.1 Thermochromatism dependent on temperature only

An effective synthetic route to improve the thermochromatic reversibility is to design and incorporate other conjugated organic moieties into side chains. For instance, Zou and Zhang *et al.* have developed a family of novel PDA materials with reversible thermochromatism by introducing azobenzene chromophores.^{23,25–27} Fig. 4 shows the chemical structures of some building azobenzene/diacetylene monomers. The azobenzene-substituted PDA films were prepared by coating the monomer solutions onto substrates followed by photopolymerization under UV light. They found that the improved intermolecular interaction (π - π stacking) among the side chains greatly enhanced the thermal stability of the PDA. As shown in Fig. 5, PDA films showed three different chromatic transitions from blue to red with an intermediate purple coloration during the heating process. For a heating temperature lower than 105 °C, the thermochromatism was reversible, *i.e.*, the red PDA returned to the original blue when cooled to room temperature. Although strong intermolecular interactions among side chains are important to the reversible thermochromatism, it was also found that PDA materials derived from 4-methoxybenzyl 10,12-pentacosadiynoate without such interactions²⁸ showed good thermochromatic reversibility. Crystallization of the long alkyl side chains may be critical to the conformation reversibility of the PDA backbone.

Thermochromatic reversibility has also been realized by increasing the hydrogen bonds of assembled PDA

materials.^{23,29–37} An efficient approach is to introduce urea units in the side chains to form two hydrogen bonds stronger than those of amides or urethanes. Moreau *et al.* first studied the PDA materials derived from compound 5 in Fig. 6 by UV-vis spectroscopy.²⁴ It was found that the color transition between purple at room temperature and red at high temperature of 70–120 °C was reversible. However, heating at temperatures higher than 130 °C produced an irreversible red. In order to further understand how the hydrogen bonds affected the thermochromatism, they also traced the structural transitions of PDA materials during the color changes by Fourier transform infrared spectroscopy. A urea unit may show three infrared absorption bands related to the N–H stretch, the C=O stretch (also called Amide I), and a combination of the above two stretches (also called Amide II). Similar to UV-vis studies, three phases were discovered. Both Amide I and Amide II linearly shifted to free states at a crucial temperature of 120 °C. At a higher temperature from 120 to 140 °C, heating dramatically affected the hydrogen bonds with highly shifted and intensity-decreased Amide I and Amide II bands. For temperatures above 140 °C, no further evolution was detected for the hydrogen bond. As a comparison, when cooled to room temperature after heating at a temperature lower than 120 °C, the Amide I and Amide II bands recovered their wavenumbers, band shapes, and band intensities. In other words, this thermal deformation of the hydrogen bonds and structural modification around the urea are reversible. Therefore, a reversible thermochromatism had been found from UV-vis spectroscopy. Fig. 7 schematically shows that the reversible molecular organization produces thermochromatic reversibility. However, when cooled from a temperature above 120 °C, no recovery was found for the FTIR bands, *i.e.*, the urea may form new hydrogen-bonded networks. This new supramolecular organization could not switch the conformation of the PDA conjugated backbone back, resulting in an irreversible thermochromatism. It should be noted that if the urea group was too close to the diacetylenic moiety (compound 6 in Fig. 6), the photopolymerization of monomers directly produced red PDA. The rigid hydrogen bonds may inhibit the polymerization and prevent the synthesis of blue PDA.

Kim *et al.* had further compared PDA materials derived from diacetylenic monomers capable of forming different

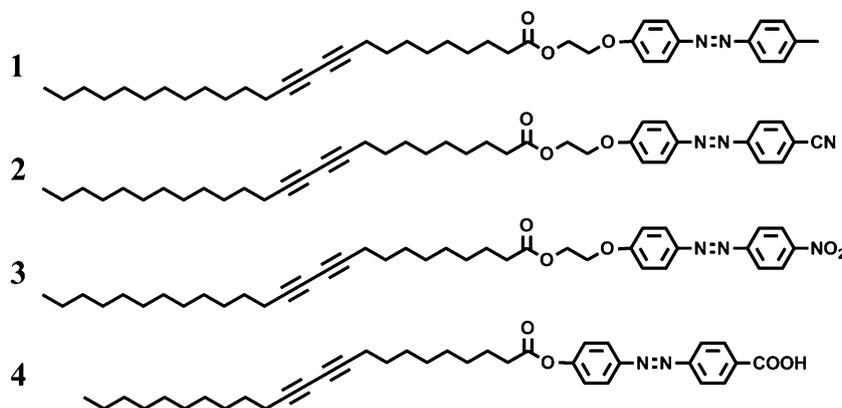


Fig. 4 Chemical structures of building azobenzene/diacetylene monomers.

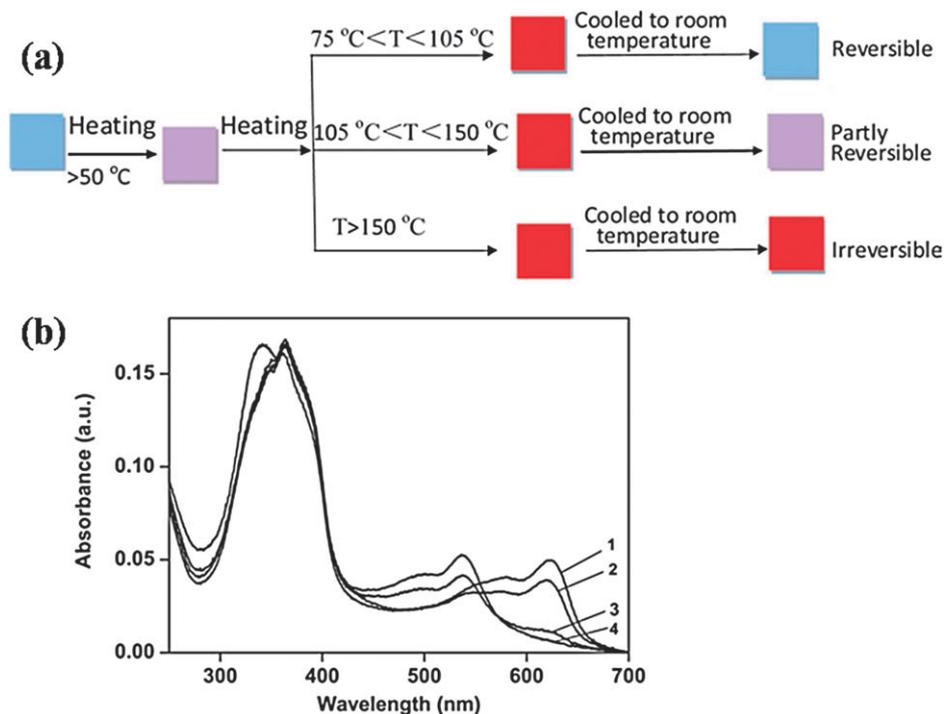


Fig. 5 (a) Schematic diagram of the thermochromic phase transition for PDA films. (b) UV-vis spectra of PDA2 films at room temperature (1) and respectively heated to (2) 90 °C, (3) 130 °C, and (4) 180 °C for 5 min under vacuum followed by cooling to room temperature before measurements. (Reproduced with permission from ref. 23. Copyright 2008, The Royal Society of Chemistry.)

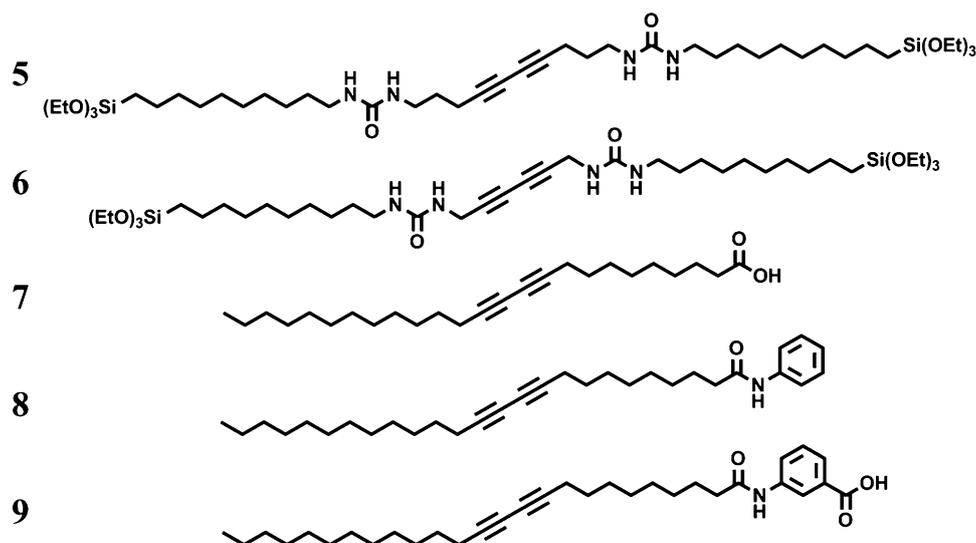


Fig. 6 Chemical structures of diacetylenic derivatives capable of forming different numbers of hydrogen bonds.

numbers of hydrogen bonds (Fig. 6).³⁰ Monomer 7 had a hydrogen-bonded carbonyl stretch, monomer 8 had hydrogen-bonded amide and carbonyl stretches, while monomer 9 possessed all of the above three stretches. When heated over 75 °C, the hydrogen-bonded carbonyl stretch for monomer 7 slightly shifted to a higher wavelength with reduced strength which did not revert after cooling to room temperature. As a comparison, monomer 9 maintained the hydrogen-bonding strength during the heating/cooling cycle. Fig. 8a further schematically shows the formation of a strong hydrogen-bonded network. Therefore,

it was found that PDA from monomer 7 exhibited irreversible thermochromatism, while PDA from monomer 9 exhibited reversible thermochromatism (Fig. 8b).

Chen *et al.* have recently fabricated PDA/poly(vinyl pyrrolidone) nanoaggregates in solutions with intriguing thermochromatic reversibility.³⁶ As shown in Fig. 9, the “bricks and mortar” morphology formed through hydrogen bonds between pyrrolidone and the side chains in PDA was believed to be responsible for the reversible thermochromatism. The above morphology may favor the full hydrogen-bonded

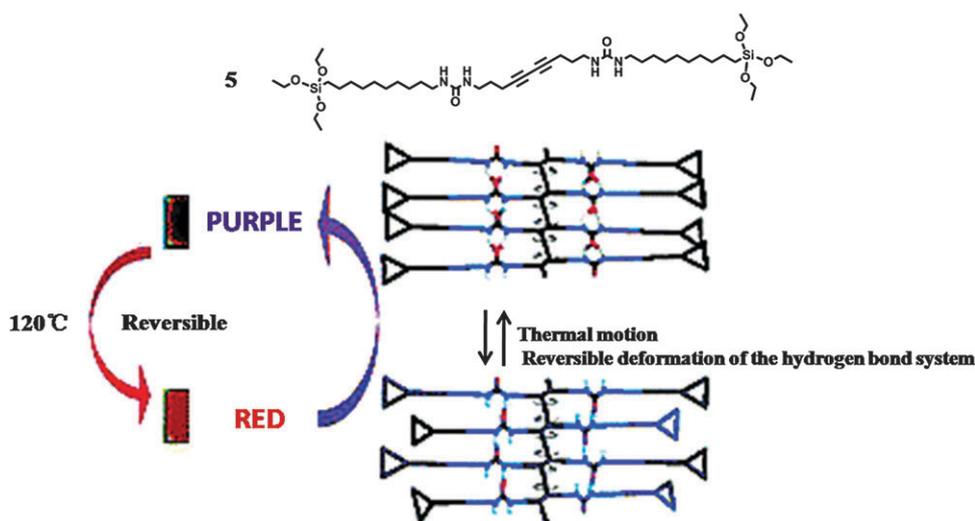


Fig. 7 Formation of strong hydrogen bonds providing PDA with thermochromatic reversibility. (Reproduced with permission from ref. 24. Copyright 2006, American Chemical Society.)

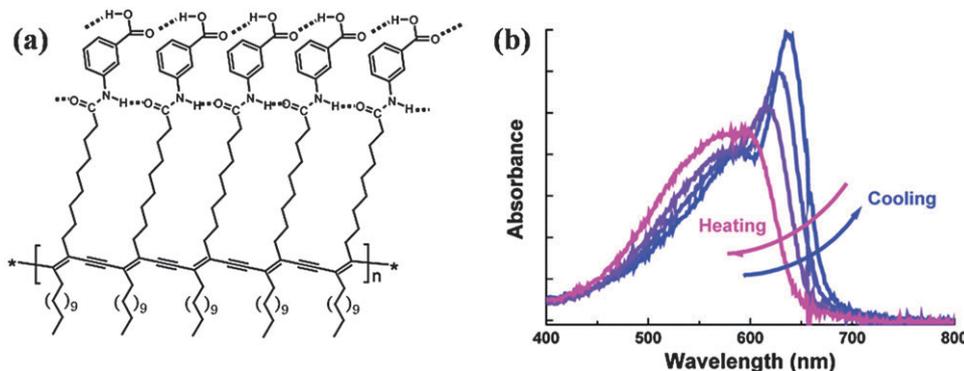


Fig. 8 (a) Schematic illustration for the formation of a strong hydrogen-bonded network. (b) UV-vis spectra of reversible thermochromatic transitions in PDA derived from monomer 9 in Fig. 6. (Reproduced with permission from ref. 30. Copyright 2003, American Chemical Society.)

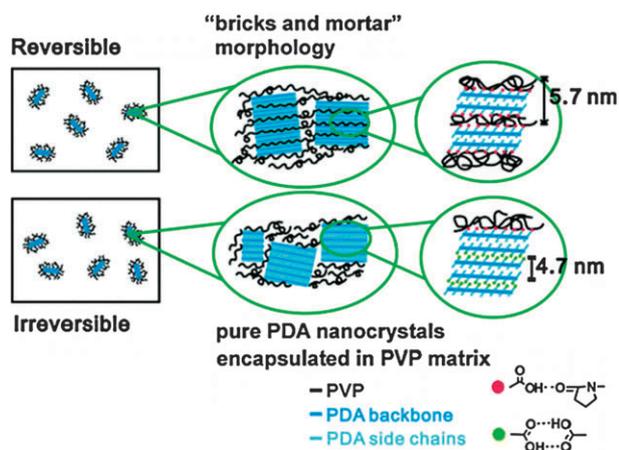


Fig. 9 Schematic illustration for a PDA material with reversible thermochromatism through the formation of a “bricks and mortar” morphology, *i.e.*, PDA nanocrystals encapsulated into a poly(vinyl pyrrolidone) matrix. (Reproduced with permission from ref. 36. Copyright 2008, American Chemical Society.)

interactions between the two polymers to provide conformational reversibility of PDA backbones as in a control experiment without the above morphology, PDA/poly(vinyl pyrrolidone) nanoaggregates exhibited irreversible thermochromatism under the same conditions.

3.2 Thermochromatism dependent on temperature and the presence of metal ions

Diene crystals show an interesting crystal structure transition according to temperature.³⁷ Inspired by the above construction, by reacting a diacetylenic acid with NaOH in aqueous solution, Pang *et al.* had firstly synthesized metastable PDA crystals through strong intermolecular interactions among side chains in PDA, which increase molecular and bond angle constraints (Fig. 10). Heating at 55–65 °C released the internal strain in the metastable PDA crystal with increasing effective PDA conjugation length, which produced an irreversible color change from red to blue. On the other hand, the electrostatic interaction converted the metastable PDA crystal to a stable

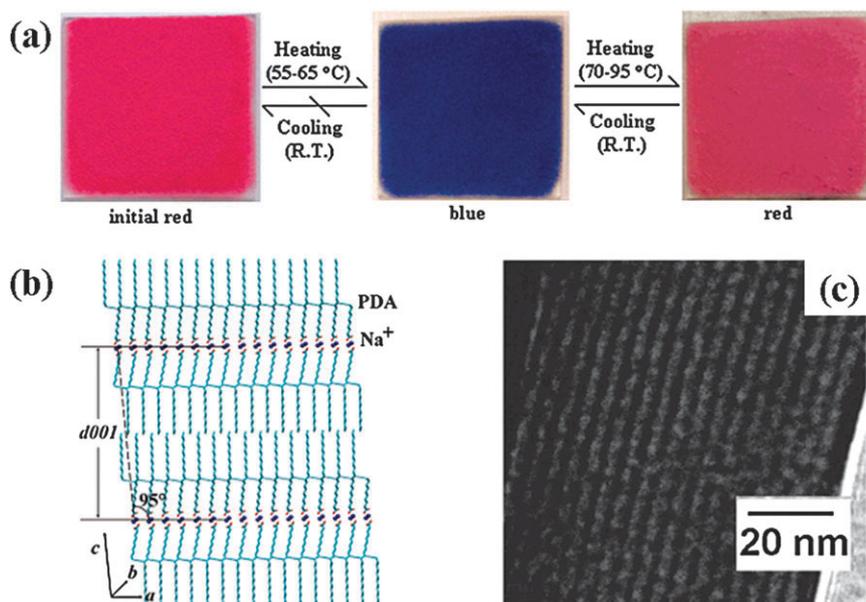


Fig. 10 Chromatic properties and structures of the PDA/Na nanocomposite. (a) Photographs of its color transitions at different temperatures. (b) Schematic illustration of the molecular structure. (c) Transmission electron microscopy (TEM) image. (Reproduced with permission from ref. 37. Copyright 2006, American Chemical Society.)

crystal with a blue-to-red reversible thermochromatism at a higher temperature range of 70–95 °C.

Liu *et al.* further systematically studied PDA films modulated with different transitional metal ions through the carboxylate anion.³⁸ They found that different metal ions formed different coordination models, which greatly affected the thermochromatic properties of the PDAs. Ag^+ -coordinated films could not even be polymerized to form PDA, Cu^{2+} -coordinated PDA films showed stable supramolecular chirality due to the helical arrangement of the polymer backbone and did not change color, while Zn^{2+} -coordinated PDA films exhibited a reversible thermochromatism between blue and purple with a possible mechanism schematically illustrated in Fig. 11. Zn^{2+} ions were coordinated with carboxylate in a bridging bidentate form. The composite film took a triclinic subcell and the alkyl chains had an all-*trans* conformation at room temperature. Once heated, the subcell changed to orthorhombic with re-organization of the PDA backbone. As a result, blue films switched to purple. During this process, the bridging bidentate head group was not

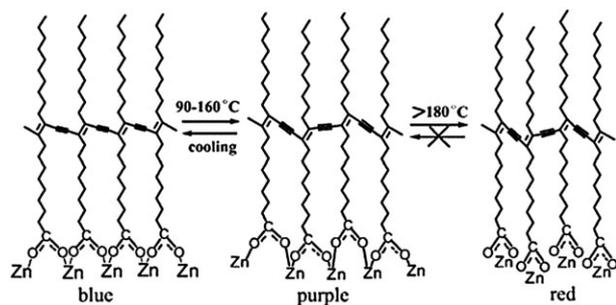


Fig. 11 Mechanism for the thermochromism of PDA/ Zn^{2+} film. (Reproduced with permission from ref. 38. Copyright 2005, American Chemical Society.)

changed significantly, so the chromatic transition between blue and purple was reversible. Due to the thermally stable Zn^{2+} -coordinated network, the derived PDA showed reversible color change up to 160 °C, the highest critical temperature reported to date.

It should be noted that, in the above systems, ions have been incorporated into the same diacetylenic monomer of $\text{CH}_3(\text{CH}_2)_{11}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$. As widely explored, the composition and length of the side chains largely affect the organization of PDA with different properties. Therefore, the conclusions need to be further confirmed or may be modified in the use of other monomers. For instance, the Zn^{2+} -coordination and PDA backbone arrangement may be different if the bridging side chain between Zn^{2+} and the diacetylenic bond varies. As a result, the derived PDA material will exhibit different chromatic properties under heating. However, to the best of our knowledge, no such comparing experiments are available, although diacetylenic monomers with tunable structures of $\text{CH}_3(\text{CH}_2)_m\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_n\text{COOH}$ (here m can be 9 or 11, and n can be 3, 4, 6, or 9) or even $\text{HOOC}(\text{CH}_2)_x\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_y\text{COOH}$ (e.g., $x = y = 8$) are commercially available.

3.3 Thermochromatism dependent on formation of organic/inorganic hybrids

Joo *et al.* had realized a reversible thermochromatism by assembling a thin PDA film on a Ag surface, and the PDA showed a reversible color change at ~ 65 °C.³⁹ Similarly, the reversible conformation change in the side chains of the PDA was believed to be responsible for the reversible color change. As shown in Fig. 12, it was found that a regular *trans*-zigzag structure existed in the side chains for a blue phase at room temperature and switched to an irregular *gauche* structure after heating at ~ 65 °C with the chromatic transition to red.

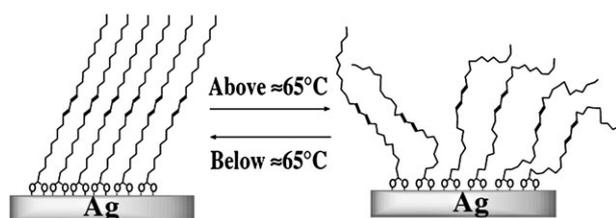


Fig. 12 Realization of reversible thermochromatism by assembling PDA film on a Ag surface. (Reproduced with permission from ref. 39. Copyright 2007, The Chemical Society of Japan.)

Once cooled to room temperature, the disordered structure reverts to the original ordered one due to substantial van der Waals interactions among the alkyl chains. However, for the same PDA on a silica substrate, we found that the thermochromatism was not reversible, so the Ag surface may also play a critical role for the thermochromatic reversibility although it was not discussed in the literature. In fact, Burns *et al.* also coated the same PDA on a silica substrate, and discovered a partially reversible transition from blue to an intermediate purple, followed by an irreversible transition to red.⁴⁰

By the formation of layered double hydroxide hybrids with PDA between two inorganic clay nanosheets, PDA nanocomposites with reversible thermochromatism at 80 °C have been synthesized.⁴¹ It was found that the PDA could be strengthened and stabilized within the rigid inorganic sheets at high temperature. For instance, X-ray diffraction patterns showed that the lamellar organic/inorganic structures were retained after heating at temperatures up to 100 °C, while the same pure PDA began to collapse into an amorphous powder at ~70 °C. Fig. 13 schematically illustrates how the hybrid structure is more thermally stable compared to that without an inorganic layer.

By assembling tetraethylorthosilicate with oligoethylene glycol functionalized diacetylenic surfactants, Lu *et al.* incorporated PDA into a robust silica network to form highly ordered organic/inorganic nanocomposites.^{42,43} The PDA nanocomposites rapidly and reversibly responded to heating over 47 °C. This was derived from the formation of hydrogen bonds between side chains in PDA and silanol moieties of the surrounding inorganic mesophase, which provides the restoring force for the recovery of the conformations of side chains.

In order to further improve the thermochromatism at higher temperatures, Peng *et al.* further developed a series of PDA/silica nanocomposites in which PDA was covalently bonded to the inorganic mesophase through the self-directed assembly of diacetylene-bridged silsesquioxanes.²⁰ It was found that PDA nanocomposites derived from $\text{CH}_3(\text{CH}_2)_{11}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ and $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCO}(\text{CH}_2)_8\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ showed reversible thermochromatism at temperatures up to 140 °C, those from $\text{CH}_3(\text{CH}_2)_9\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_6\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ and $\text{CH}_3(\text{CH}_2)_{11}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ were partially reversible under the same conditions, while the PDA nanocomposite from $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCOOCH}_2\text{C}\equiv\text{C}-\text{C}\equiv\text{CCH}_2\text{COONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$

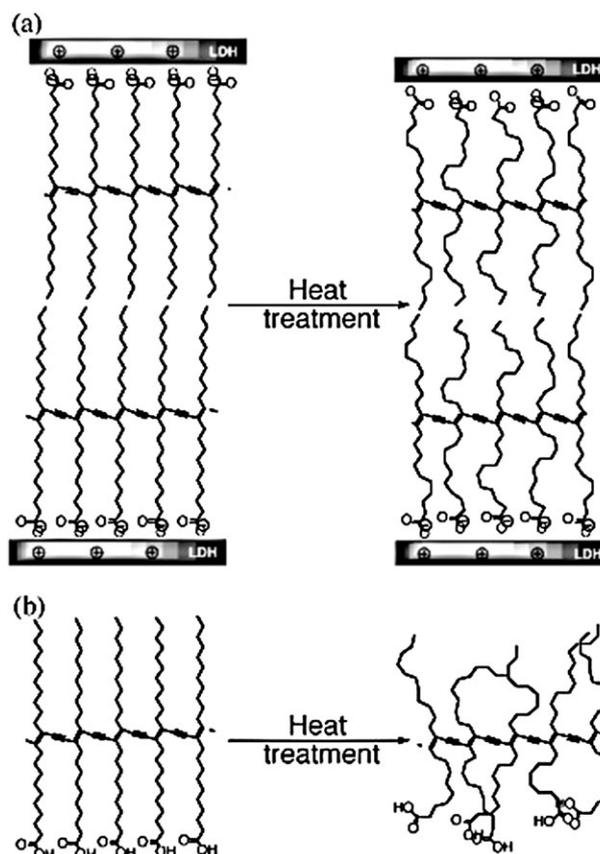


Fig. 13 Schematic comparison for the structural change under heating between (a) PDA incorporated into inorganic clay nanosheets and (b) pure PDA without incorporation into the above nanosheets. (Reproduced with permission from ref. 41. Copyright 2005, American Chemical Society.)

was totally irreversible. The flexibility in side chains was believed to be responsible for the above different thermochromatic behaviors. The mentioned five monomers have decreasing numbers of carbon atoms (8, 8, 6, 3, and 1, respectively) between the diacetylenic moiety and the amide group, which gives the resulting PDAs with decreasing side-chain flexibility. Therefore, the PDA/silica nanocomposites showed thermochromatisms from reversible to partially reversible and to completely irreversible.

Besides the formation of solid PDA/silica nanocomposites, it was also possible to produce mesoporous nanocomposites by co-assembling diacetylene-bridged silsesquioxane with surfactant.⁴⁴ For instance, Fig. 14 shows the co-assembly of $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCO}(\text{CH}_2)_8\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ with the surfactant cetyltrimethylammonium bromide, followed by removal of surfactant. Transmission electron microscopy and X-ray diffraction indicated a highly ordered hexagonal mesostructure for the resulting porous nanocomposite. As expected, the mesoporous PDA can rapidly and reversibly responded to heating with temperatures up to 140 °C. For the mesoporous PDA, another interesting sensitivity lies in that it could more quickly respond to solvents compared to the solid PDA. For instance, it was found that the mesoporous PDA completed the response to a

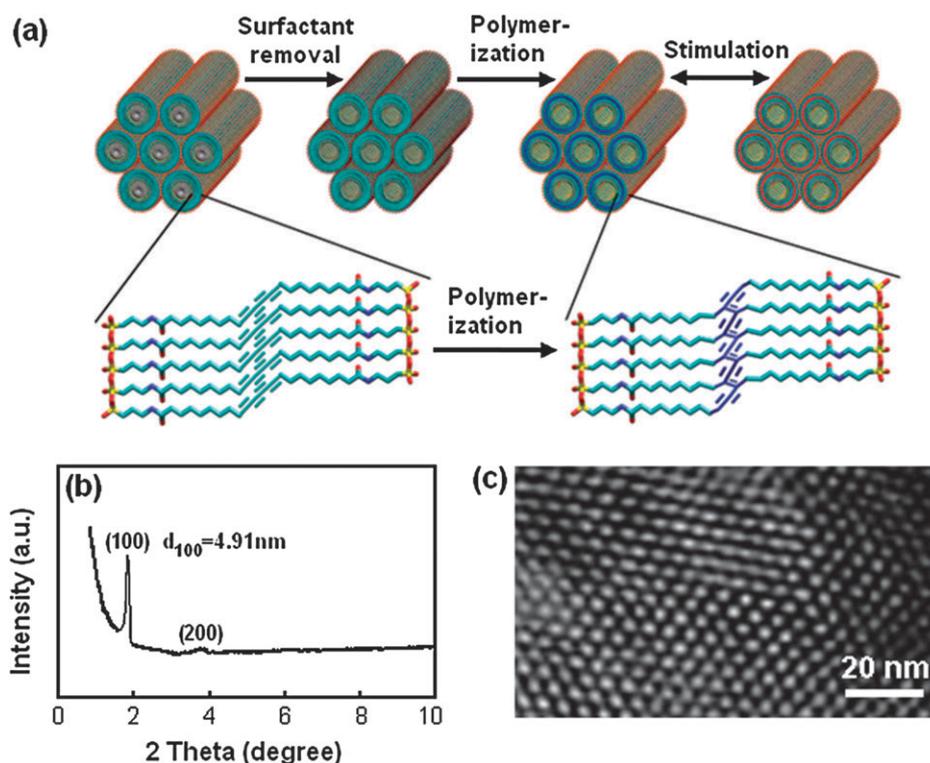


Fig. 14 The formation of mesoporous PDA/silica nanocomposite with reversible thermochromatism through the co-assembly of a diacetylene-bridged silsesquioxane and the surfactant cetyltrimethylammonium bromide. (a) Schematic illustration. (b) X-Ray diffraction pattern. (c) TEM image. The used silsesquioxane is $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCO}(\text{CH}_2)_8\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$. (Reproduced with permission from ref. 44. Copyright 2006, American Chemical Society.)

methanol mixture in minutes while the nonporous PDA needed hours for the same process (Fig. 15).

4. Polydiacetylene with reversible chromatism induced by pH

Besides the widely explored reversible thermochromatism, there are also several PDA systems which showed reversible chromatic transition in response to the external pH.^{45–47} Jonas *et al.* have pioneered this direction and fabricated novel PDA lipids based on hydrazide derivatives, and these hydrazide lipids underwent a reversible color change between blue and red when the surrounding pH varied between acidic and basic

conditions (Fig. 16).⁴⁵ Similar to many PDA systems with reversible thermochromatism, it was shown that this reversible chromatic transition was also attributed to the unique hydrogen-bonding pattern of the hydrazide headgroups. They have two different hydrogen-bonding motifs with one sensitive to pH while the other is not. The above hydrogen bonds have been traced by Fourier transform infrared spectroscopy under acidic and basic conditions. The results showed that the bonding structures strongly varied between the neutral hydrazide and the HCl salt. As the lipid was not adversely affected during the change in pH, the alternations in bonding structures caused only subtle changes in lipid packing, allowing the reversible chromatic transition. Based on the same

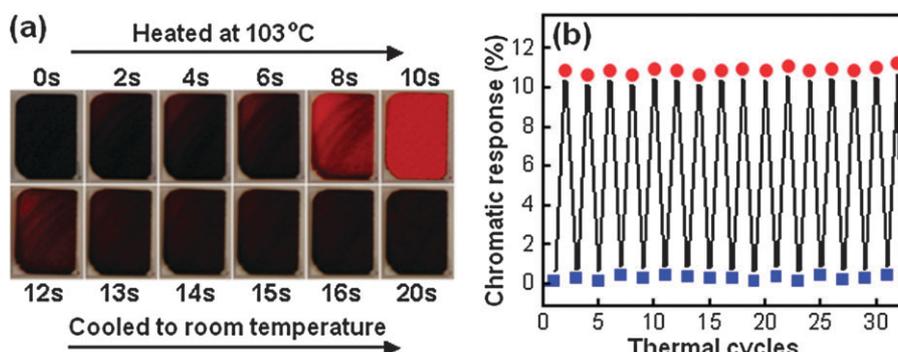


Fig. 15 Rapid and reversible thermochromatism in the mesoporous PDA nanocomposite film. (a) Photographs. (b) CR values at 25 and 103 °C for a series of thermal cycles. (Reproduced with permission from ref. 44. Copyright 2006, American Chemical Society.)

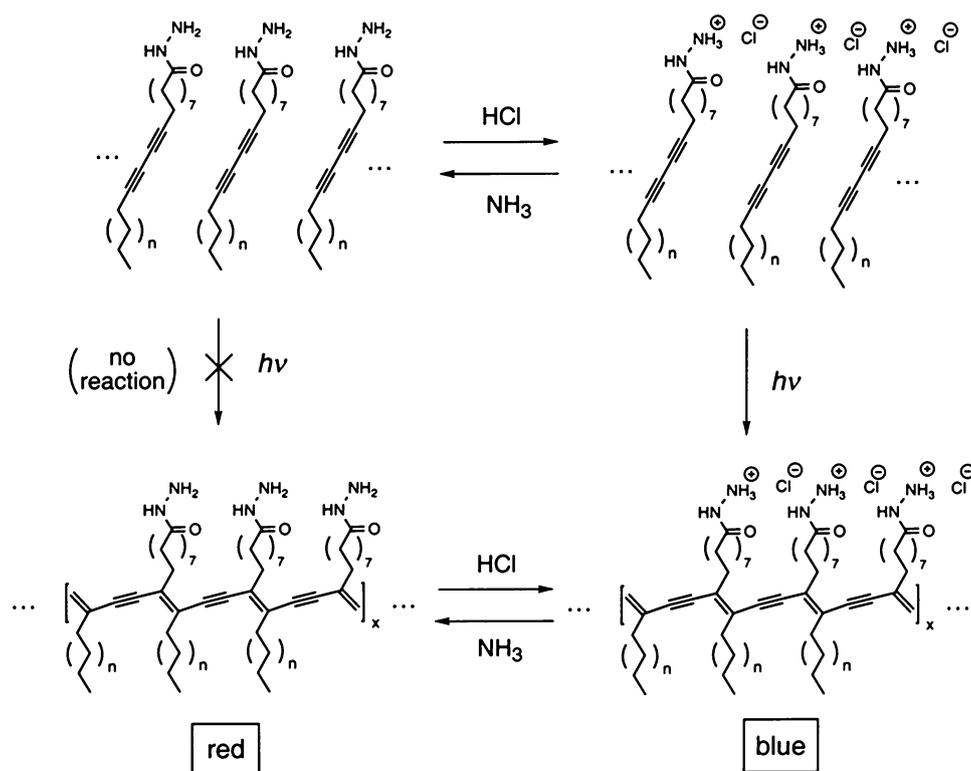


Fig. 16 Schematic illustration of the polymerization behavior of the diacetylene hydrazide lipids and the colorimetric changes of the resulting PDA lipids in the presence of HCl or NH_3 . (Reproduced with permission from ref. 45. Copyright 1999, American Chemical Society.)

molecular design, Lee *et al.* further synthesized PDA films with reversible responses to pH changes by using hydrazide head groups instead of acid heads that provide four hydrogen-bonding sites and could also be altered by protonation of the terminal nitrogen.⁴⁶

5. Light-induced reversible chromatic transition of polydiacetylene

Although PDA has been extensively investigated to chromatically respond to heating, pH, and chemicals, few studies have been made on light-induced chromatic transition in PDA. On the other hand, light-induced chromatic transition in PDA materials may exhibit a wide variety of applications as it can be safely, readily, and accurately performed. Recently, Peng *et al.* have realized the light-induced chromatic transition of PDA nanocomposite films by incorporation of azobenzene moieties, which are well-known as photoactive systems with a unique conformation transition between *trans* and *cis* under UV irradiation.⁴⁸ As shown in Fig. 17, azobenzene formed an alternated lamellar mesostructure with PDA. For a *trans*-to-*cis* switch, azobenzene moieties become shorter and may pull neighboring side chains of PDA. The re-arrangement of side chains decreased the effective conjugation length of the PDA backbone which produced a color change from blue to red. The speed for the chromatic transition under UV light strongly depended on the length of the side chains in PDA, which played a critical role for the transfer efficiency of the conformation change from the azobenzene to PDA. Shorter side chains favor faster and more efficient

transfer. The derived PDA/azobenzene nanocomposite from $\text{CH}_3(\text{CH}_2)_9\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_3\text{COOH}$ completed the color change much faster compared to that from $\text{CH}_3(\text{CH}_2)_9\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_4\text{COOH}$, while almost no color changes were observed for the nanocomposites derived from $\text{CH}_3(\text{CH}_2)_{11}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$. Unfortunately, the above UV-induced chromatic transition was not reversible, *i.e.*, the red PDA film did not revert to the original blue once azobenzene switched back from *cis* to *trans* under UV light with a longer wavelength.

In order to improve the chromatic sensitivity and reversibility of PDA, Zou *et al.* synthesized a series of azobenzene-incorporated PDAs through chemical bonds between azobenzene and the PDA backbone.⁴⁹ The derived PDA vesicles were fabricated to achieve a faster chromatic switch from blue to red in response to photonic stimuli (wavelength of 365 nm), *e.g.*, 10 min compared to hours for the above azobenzene-incorporated PDA film by Peng *et al.* However, subsequent UV irradiation at 435 nm did not induce red PDA vesicles back to blue either. It was found that strong π - π stacking interactions among azobenzene chromophores and the formation of a conjugated polymer chain ensured 'locking' of side chain configurations, and 'inhibition' of the photo-isomerization of the azobenzene chromophore at room temperature. Therefore, they also introduced pure PDA without azobenzene into the above vesicles to break the π - π stacking interactions among azobenzene during the preparation. The modified PDA vesicles exhibited blue-to-red transition under UV irradiation of 365 nm, and the above chromatic transition was partially reversible under another longer-wavelength UV irradiation of

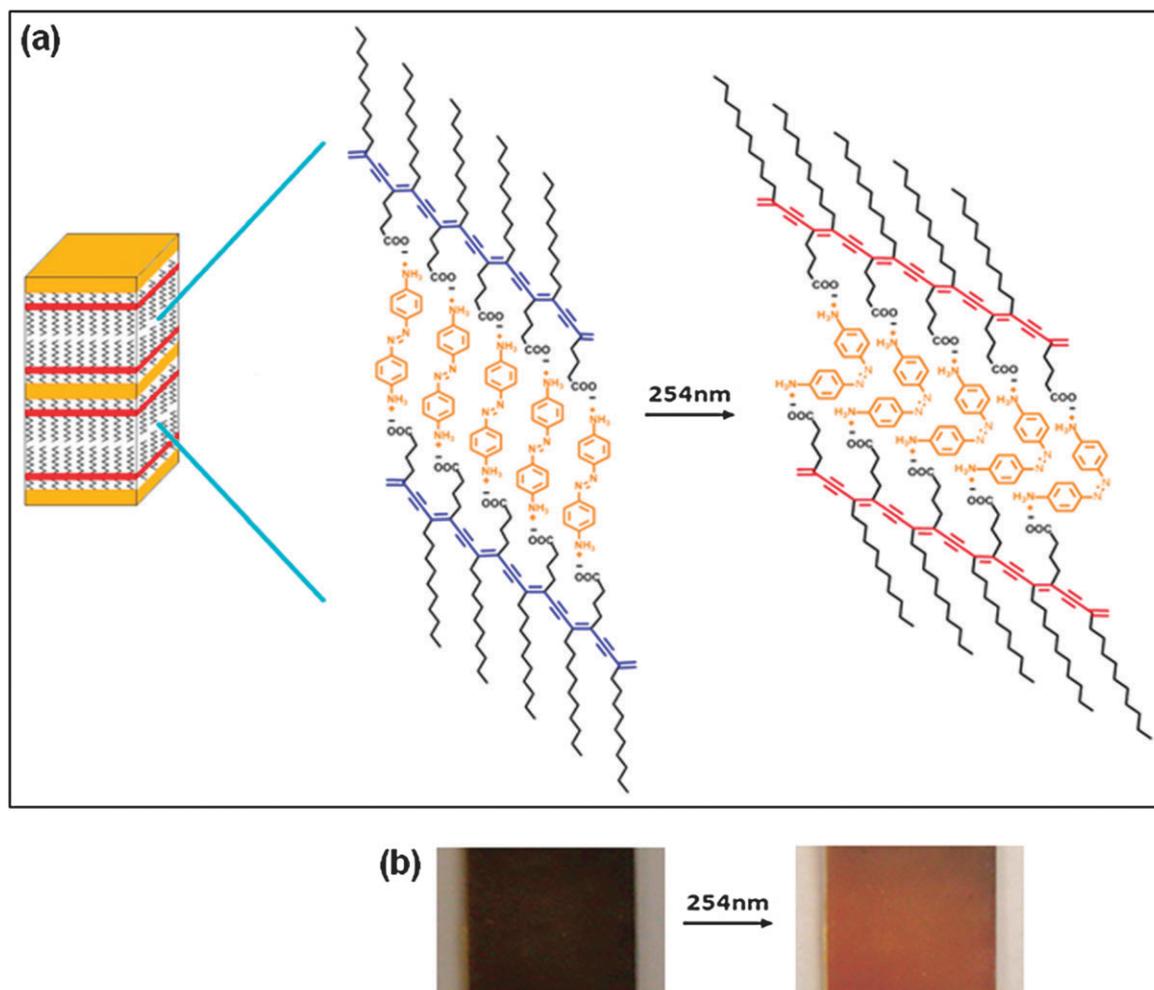


Fig. 17 UV-induced chromatic transition of a PDA/azobenzene nanocomposite by assembling 4,4'-azodianiline and 5,7-octadecadiynoic acid. (a) The *trans*-to-*cis* transition in azobenzene under UV irradiation inducing the conformation change in PDA with a color change. (b) Photographs of the blue and red film. (Reproduced with permission from ref. 48. Copyright 2010, American Chemical Society.)

435 nm. Fig. 18 schematically illustrates the above chromatic transition induced by the photo-isomerization of azobenzene under UV irradiation with different wavelengths.

To further improve the chromatic reversibility under UV light, Zou *et al.* fabricated a reversible assembly system through the use of α -cyclodextrin (α -CD).⁵⁰ Driven by hydrophobic and van der Waals interactions, the *trans*-azobenzene can be well-recognized by α -CD. However, when the *trans*-azobenzene is transformed to the *cis*-azobenzene, α -CD cannot include the bulky *cis* form any more due to the mismatch between the host and guest. Therefore, the host-guest assembly and disassembly between the azobenzene and α -CD by an external photo-stimulus can act as a driving force to induce a chromatic transition of the azobenzene containing PDA vesicles. The above reversible assembly under UV irradiation is schematically illustrated in Fig. 19(a). Fig. 19(b) further shows the obvious blue-to-red color transition for the vesicle solution upon mixing with α -CD solution. This colorimetric transition can be ascribed to the inclusion reaction of α -CD with the vesicles. Subsequently upon irradiation with 365 nm light for 30 min, the red vesicles solution turned back to dark blue. This can be ascribed to the disassembly of α -CD and the

guest molecules, and the changes in conformation order of the side chain within the PDA matrix induced by α -CD could be completely recovered.

To date, the light-induced chromatic transition in PDA has been mainly realized by incorporation of azobenzene moieties. Based on the above chromatic mechanism, the other organic isomers which can also switch conformations between *trans* and *cis* should be able to provide the similar functionality. In addition, as the transition between *trans* and *cis* may be driven by many other stimuli such as change in pH and existence of specific chemicals, the derived PDA can change color under stimulation of pH or chemicals in addition to light as discussed above.

6. Reversible electrochromism of polydiacetylene

Besides UV light, great efforts have also been made to explore PDA with other new sensing functionalities such as current-induced chromatic transition which should be able to be realized according to the mechanism of the color change in PDA. However, it is difficult to induce conformation changes in pure PDA by electric current partially because it

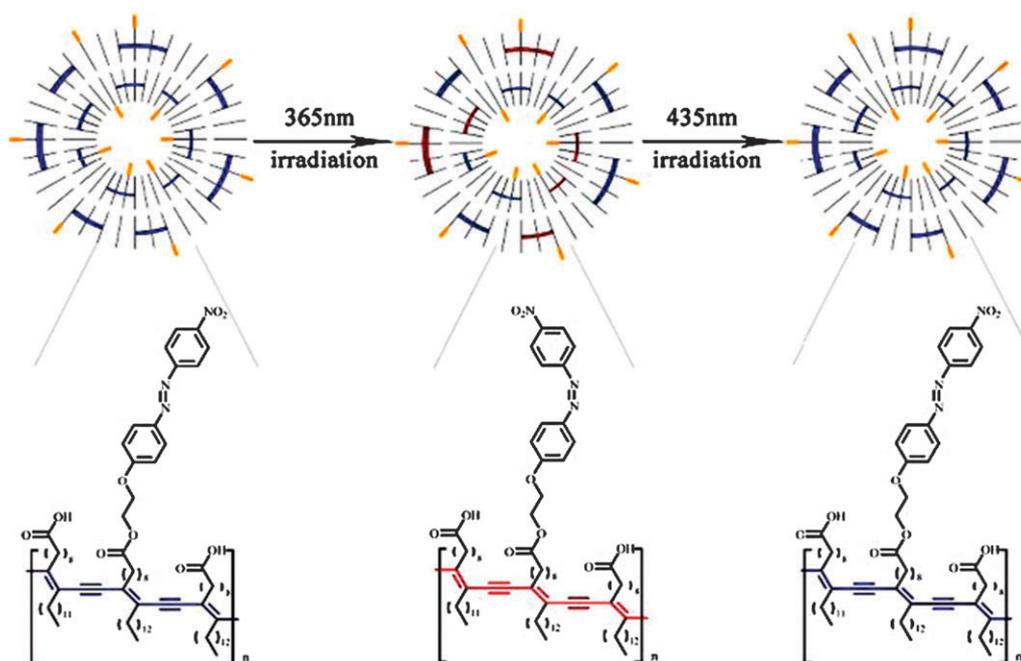


Fig. 18 PDA nanocomposite vesicle with azobenzene moieties chemically bonded to PDA side chains showing partially reversible chromatic transition under UV light. (Reproduced with permission from ref. 49. Copyright 2009, Elsevier B.V.)

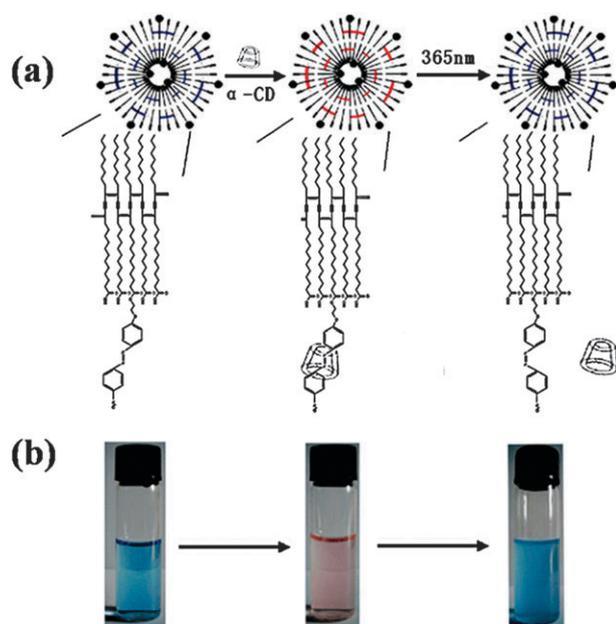


Fig. 19 PDA vesicle with reversible chromatic transition under UV light by incorporation of both azobenzene and α -cyclodextrin. (a) A scheme showing that inclusion and exclusion reactions of α -cyclodextrin in azobenzene are responsible for the reversible color change under UV light with different wavelengths. (b) Photographs of the blue and red PDA vesicle solution. (Reproduced with permission from ref. 50. Copyright 2009, The Royal Society of Chemistry.)

does not have good electrical conductivity. On the other hand, current-induced chromatic transition can be very promising for a broad spectrum of applications from aircraft to small electronic facilities, *e.g.*, *in situ* sensing monitors and evaluation.

Similar to the above PDA materials with reversible chromatic transition in response to either heating, pH, or UV light, a possible and convenient approach to realize the electrochromatism is to form nanocomposites. If one phase produces strong electric fields to induce conformation changes in incorporated PDA molecules, the PDA nanocomposite may show an intriguing electrochromatism. One of the ideal candidates to meet this requirement are carbon nanotubes which show excellent electrical conductivity.^{51,52} By incorporation of nanotubes into PDA, Peng *et al.* developed a family of novel nanocomposite fibers with electrochromatism.⁵³

As expected, nanotube/PDA composite fibers changed color from blue to red when passed with current. Fig. 20 exhibits the experimental setup and chromatic transition for a composite fiber with a diameter of 11 μm . The minimum current to induce the color change is 10 mA, and the electrochromatic property strongly depended on the current value. For instance, the blue-to-red transition was reversible at currents lower than 30 mA while irreversible at higher values. Most importantly, compared to the reversible chromatic transition induced by heating, pH, or light, the electrochromatism could be much faster, typically less than 2 s.

The current-induced color change was concluded more likely from interactions between nanotubes and PDA and excellent electrical conductivities of composite fibers with three-dimensional hopping conduction model where electrons hop from one nanotube to the neighboring ones. Therefore, when passed with currents, PDA/nanotube fibers produced electric fields among the nanotubes, which resulted in polarization of polar side chains in PDA. The above polarization induced the conformation change in PDA with chromatic transitions. For low currents, the PDA backbone could return to the original conformation upon removal of current, so a reversible color change was observed. However, higher currents may destroy the recovery capability of the PDA conformation.

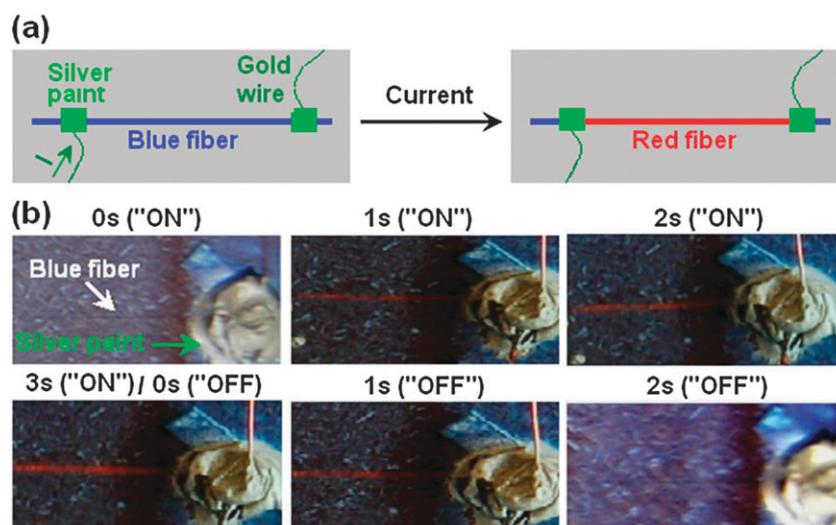


Fig. 20 Electrochromatic PDA/carbon nanotube composite fiber. (a) Experimental setup. (b) Rapid and reversible color changes of a composite fiber in response to electric current. (Reproduced with permission from ref. 53. Copyright 2009, Nature Publishing Group.)

To the best of our knowledge, only one electrochromatic PDA system has been reported by use of carbon nanotubes. As electric fields among carbon nanotubes are responsible for the conformation change of PDA, it is possible to realize electrochromatism of PDA by incorporation of many other conducting nanomaterials, *e.g.*, arrays of metal nanowires/nanotubes or conducting polymer nanorods which have been extensively investigated.

7. Conclusions

PDA has been extensively studied and proposed as sensing materials as early as the 1970s with a large number of publications and patents, however, few practical applications are available. In order to improve the practical applications of PDA materials, it is necessary to enhance their chromatic reversibility and sensitivity to more external stimuli. This tutorial review has summarized the recent development in the synthesis of reversible PDA systems in response to both widely explored stimuli of heating and pH and two new stimuli of UV light and electric current.

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