

Chromatic Studies of a Polymerizable Diacetylene Hydrogen Bonding Self-Assembly: A “Self-Folding” Process To Explain the Chromatic Changes of Polydiacetylenes

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Received January 11, 1999. In Final Form: March 9, 1999

In the present study, a new diacetylene compound (PDATAZ), which readily forms a complementary hydrogen bonding self-assembly at the air–water interface or in the solid state with barbituric acid (BA) or cyanuric acid (CA), was designed and synthesized. The photopolymerization studies of PDATAZ and its assembly with BA or CA have revealed some important insights on the chromatic properties of polydiacetylenes. It was found that the chromatic property of polydiacetylenes is determined by whether the polymer chain is capable of adopting a linear chainlike shape. With the continuous increase of the length of the polymer chain, the original linear polyenyne backbone starts to “self-fold” to a “zigzag” structure due to the free rotation of single bonds within the polymer chain. The efficient π -electron delocalization along the polyenyne backbone is interrupted by this process, leading to a chromatic change from the blue to red form of polydiacetylenes. If there are strong intermolecular interactions existing between the polar groups of the side chains, such as the complementary hydrogen bonding network between the triaminotriazine (TAZ) moiety of the diacetylene amphiphile and its complementary components, the movement of the side chains is restricted and the folding process of the polymer backbone is inhibited. The polymer backbone is able to maintain its extended chainlike conformation, leading to only the blue form absorption band.

Introduction

Among the different intermolecular interactions (e.g. electrostatic, hydrogen bonding, van der Waals, and π - π stacking), the strength, directionality, and selectivity of hydrogen bonding places it at the center of many research efforts aimed at the design of supermolecules and crystal engineering.¹ As one notable example, the complementary hydrogen bonding self-assembly between melamine and barbiturates or cyanurates in the solid state and solution has caused extensive attention.² Through complementary hydrogen bonding between one component that has a “donor–acceptor–donor” triad and another component that has a complementary “acceptor–donor–acceptor” array, highly organized supramolecular structures, such as linear tapes, crinkle tapes, or rosettes, are formed when these components are mixed.

More recently, it has been shown that hydrogen bond directed self-assembly at the air–water interface is as efficient as that in nonpolar organic solvent. Triamino-

triazine (TAZ) amphiphiles bearing C₁₂ or C₁₈ side chains (2C₁₂TAZ or 2C₁₈TAZ) form highly organized 1:1 hydrogen-bonded networks at the air–water interface with complementary components such as barbituric acid (BA), cyanuric acid (CA), or barbital (BT) from the aqueous subphase.^{3,4} A C₁₈ alkyl chain modified barbituric acid lipid was found to form a hydrogen bonding network at the interface with a complementary triaminopyrimidine, as well.⁵ While Langmuir and Langmuir–Blodgett film techniques have been important methods to produce highly organized structures in 2-D complementary to 3-D crystal engineering, these studies open an important new approach to the design of supermolecules in 2-D.

Polydiacetylenes are the most widely investigated class of conjugated polymers for third-order nonlinear optical effects,⁶ since their preparation was first reported in 1969 by Wegner.⁷ Diacetylenes substituted with various side chains readily undergo photopolymerization to form an ene–yne alternated polymer chain upon UV irradiation (254 nm) in a wide range of organized structures, such as single crystals,⁸ Langmuir–Blodgett films,⁹ self-assembled monolayers,¹⁰ liposomes or vesicles,¹¹ and solu-

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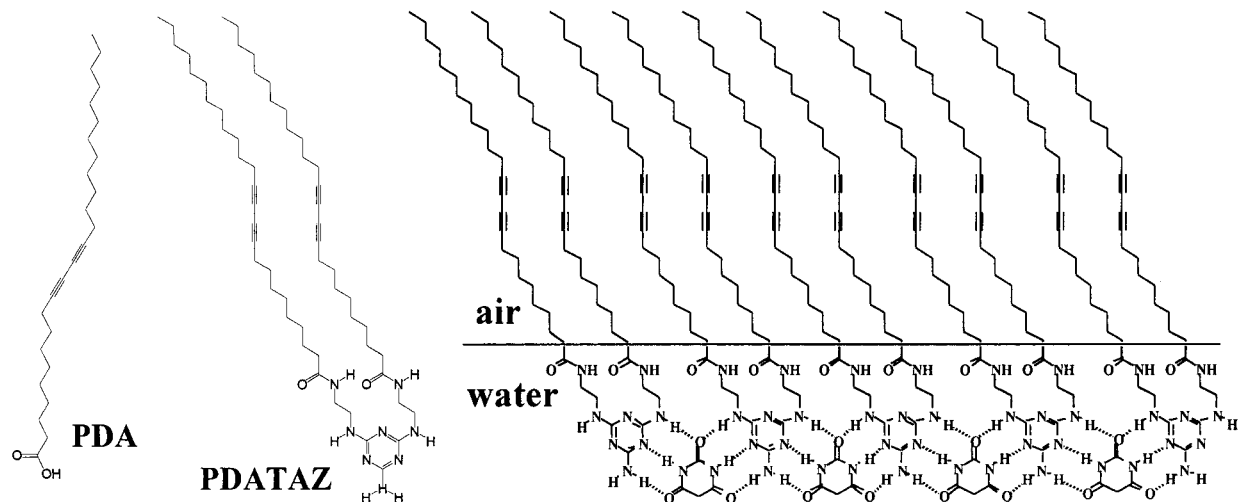


Figure 1. Illustration of the hydrogen bonding network formed between PDATAZ and BA at the air–water interface.

tions.¹² The one-dimensional conjugated polyenyne backbone exhibits large nonlinear optical susceptibilities comparable to inorganic semiconductors with ultrafast response time.^{6,13} The conjugated polydiacetylene backbone has two spectroscopically distinct phases, designated as the blue and the red forms, that result from their exciton absorption peaks at ca. 640 and 540 nm, respectively.¹⁴ Under external perturbation, such as heat¹⁵ or mechanical stress,¹⁶ the conjugated polyenyne backbone can undergo a drastic reversible color transition or irreversible color change from the blue to the red form. This unique chromatic property has made polydiacetylenes promising candidates in the development of biosensors.¹⁷

The present study has attempted to reveal the effect of a complementary hydrogen bonding network on the photopolymerization and chromatic properties of polydiacetylenes. A polymerizable diacetylene compound (PDATAZ), in which two hydrophobic 10,12-pentacosadiynoic acid (PDA) chains are attached to a TAZ headgroup through ethylenediamine linkers, was designed

and synthesized. It is expected that this amphiphile also forms 1:1 hydrogen bonding networks with BA or CA from the aqueous subphase, as shown in Figure 1, like other triaminotriazine amphiphiles.^{3,4} The effect of the formation of such a highly organized network structure on the photopolymerization of diacetylenes has been examined both at the air–water interface and in the solid state. These studies have led to a revisiting and novel interpretation of the chromatic properties of polydiacetylenes.

Experimental Section

Materials. Cyanuric chloride, ethylenediamine, barbituric acid (99%), and cyanuric acid (98%) were purchased from Aldrich Chemical Co. and used in organic synthesis or monolayer studies directly. 10,12-Pentacosadiynoic acid (PDA) was purchased from GSF Chemical Co. (Powell, OH) and recrystallized from petroleum ether before use. All organic solvents for the synthesis and purification were purchased from Fisher Scientific Co. as reagent grade and were used without further purification. 2-Amino-4,6-dichloro-1,3,5-triazine was prepared from cyanuric chloride and anhydrous ammonia according to the literature.^{2e} (10,12-Pentacosadiynoic amido)ethylamine was prepared from the succinamidyl ester of 10,12-pentacosadiynoic acid and ethylenediamine.^{11b} The ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were obtained from a Varian VXR 400 MHz spectrometer. High-resolution mass spectra were conducted by the University of Illinois, School of Chemical Sciences. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. The same apparatus was also used for the observation of color transitions or changes of polydiacetylenes.

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Synthesis and Characterization of 2-Amino-4,6-bis-(10,12-pentacosadiyn amido)ethylamino]-1,3,5-triazine (PDATAZ). To a solution of 2-amino-4,6-dichloro-1,3,5-triazine (80 mg, 0.5 mmol) in acetone (5 mL), was added (10,12-pentacosadiyn amido)ethylamine (410 mg, 1.0 mmol) in one portion. Under vigorous stirring, aqueous sodium carbonate (20 mL, 318 mg, 3.0 mmol) was added dropwise. The reaction mixture was brought to reflux overnight, shielding from lights. After cooling to ca. 40 °C, the reaction mixture was filtered, and the solids were washed with a few portions of acetone and hot water and then vacuum-dried. The bluish solids were further purified by double recrystallization from hot butanol with a yield of 20% as white solids. Mp: 138–142 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.85 (t, 6H), 1.14–1.62 (m, 66H, with 1H₂O), 2.13 (t, 4H), 2.21 (t, 8H), 3.35, 3.48 (m, 8H), 4.75 (b, 2H), 5.17 (b, 2H), 6.36 (b, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 14.0, 19.0, 22.6, 25.5, 28.18, 28.24, 28.64, 28.73, 28.78, 28.96, 29.03, 29.10, 29.20, 29.34, 29.50, 31.80, 36.70, 40.20, 65.15, 65.24, 166.77, 173.52. High-resolution FAB (+)-MS (*m/z*): calcd 924.7656, found 925.7734 (M⁺+1). Combustion Anal. Calcd for C₅₇H₉₆N₈O₂·1H₂O: C, 72.53; H, 10.39; N, 11.88. Found: C, 72.51; H, 10.49; N, 11.69.

Methods for Surface Pressure–Area Measurements and UV–Vis Absorption Spectroscopy Studies at the Air–Water Interface. HPLC grade chloroform was obtained from Fisher Scientific Co. Pure PDA or PDATAZ was dissolved in chloroform to a concentration of 1.0 mM. The water used for the monolayer study was purified by a Modulab 2020 water purification system (Continental Water Systems Corp., San Antonio, TX). The water has a resistance of 18 MΩ·cm and a surface tension of 72.6 mN/m at 20 °C. The pH values of the subphases were measured with an Accumet model 10 pH meter from Fisher Scientific Co. before use. For the subphase of pure water, 10 mM BA, and 10 mM CA, the pH values were 5.70, 2.82, and 3.85, respectively. The injected volume was 60 μL for the PDA solution (1.0 mM) and 35 μL for PDATAZ solution. After the sample was spread, the solvent was allowed to evaporated for 10 min. The compression rate was set at 5 (Å²/molecule)/min for PDA monolayer and 8 (Å²/molecule)/min for PDATAZ and PDA/PDATAZ mixed monolayers.

All the experiments were conducted in a clean room class 1000 where the temperature (20 ± 1 °C) and the humidity (50 ± 1%) were controlled. The Langmuir trough used for the surface pressure measurements was a KSV minitrough, model 2000. The trough dimensions were 7.5 cm × 30 cm. The surface pressure was measured by the Wilhelmy method. The sensitivity of the Wilhelmy plate was ±0.01 mN/m. All the isotherm measurements were repeated three times, and the isotherm presented is the average of three measurements. The difference between the average isotherm and any of the three individual isotherms is ±1 Å²/molecule. UV–vis spectra of the monolayer at the air–water interface were measured using a modified Hewlett–Packard 8452A diode array spectrophotometer through the quartz window in the center of the KSV minitrough. The UV lamp of the spectrophotometer is also the light source for the irradiation. The power of the light on the monolayer at 254 nm is 0.6 W/m².

Method for Thermochromatic Studies of Polymerized PDA, PDATAZ, and the PDATAZ-BA Self-Assembly in the Solid State. The PDA and PDATAZ solid samples were crystallized from hot petroleum ether and butanol, respectively, as microcrystalline solids. The PDATAZ-BA self-assembly was prepared by mixing the two components in a 1:1 molar ratio in hot THF solution. After cooling, the precipitates were collected and vacuum-dried. The melting points for PDA, PDATAZ, and the PDATAZ-BA self-assembly are 62–63, 138–142, and 190–195 °C, respectively. The narrow range and higher melting point of the PDATAZ-BA assembly other than pure PDATAZ indicates the formation of a complementary hydrogen bonding network between PDATAZ and BA. For photopolymerization, each of the

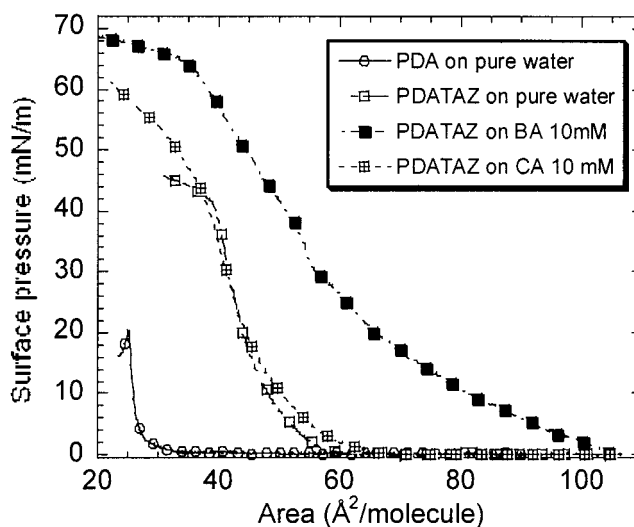


Figure 2. Surface pressure–area isotherms of PDA and PDATAZ on different subphases.

above dry solid samples (20 mg) was placed on the surface of a watch glass and irradiated for different periods of time with a Spectroline UV lamp (254 nm), which was placed about 10 cm above the sample. All samples turned from white to blue within a few seconds of irradiation. After 30 min of irradiation, the PDA sample changed to a red-brown color, while the PDATAZ and PDATAZ-BA self-assembly remained as dark blue solids even after 15 h of irradiation. All the polymerized samples are insoluble in most organic solvents. However, the polymerized PDA yielded red precipitates in chloroform while the PDATAZ and PDATAZ-BA assembly polymers remained as blue precipitates in chloroform. For thermochromatic studies, the polymer samples (after irradiation 15 min, blue form) were placed in capillary tubes and the temperatures of the color transition or change were observed through a Thomas-Hoover melting point apparatus with naked eyes.

Results

Surface Pressure–Area Isotherms. The surface pressure–area isotherms show that the PDATAZ amphiphile forms stable monolayers on the water subphase as well as on 10 mM BA and 10 mM CA subphases (Figure 2). The limiting molecular areas obtained thus are 52, 90, and 48 Å²/molecule, respectively, very close to the limiting molecular areas of 2C₁₈TAZ on these subphases.⁴ The limiting molecular area of PDATAZ on the water subphase indicates the existence of two alkyl chains. The different behavior of PDATAZ on BA and CA subphases is in agreement with the previous measurements on the 2C₁₈-TAZ amphiphile discussed previously.

The surface pressure–area isotherms of mixed PDA/PDATAZ monolayers with different ratios on water subphase have also been measured (Figure 3). The π -*A* isotherm of PDA agrees with prior literature results.^{9e,f,g,i,p} Kinetic studies showed that the PDA monolayer on the pure water subphase (pH 5.8) is not stable. The other monolayers, including the pure PDATAZ and mixed monolayers in different ratios, are all very stable at surface pressures before collapse. As one notices, when PDA is the major component of the mixed monolayer (PDA/PDATAZ 4/1, 10/1, 20/1), the collapse surface pressures are significantly increased, while there is a slight decrease of the collapse surface pressure when PDA is not the major component (PDA/PDATAZ 1/1, 1/4, 1/10). The increase of the collapse surface pressure is probably due to reorganization with tighter molecular packing of the amphiphiles.¹⁸

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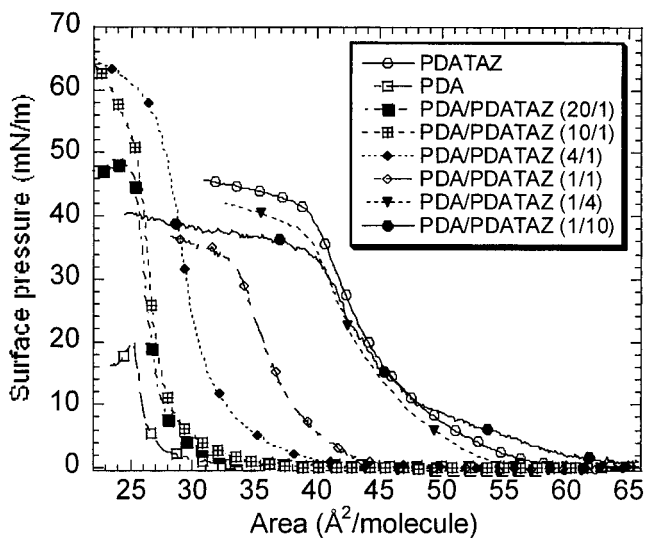


Figure 3. Surface pressure–area isotherms of PDA/PDATAZ mixed monolayers on the pure water subphase.

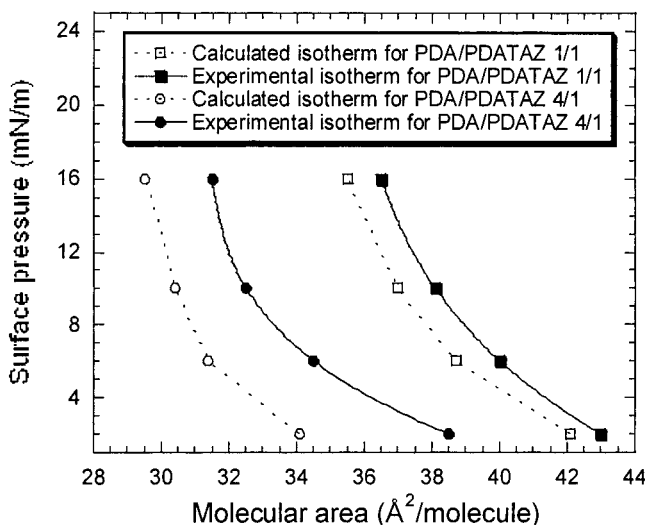


Figure 4. Miscibility studies: the calculated surface pressure–area isotherms of 1/1 and 4/1 mixed PDA/PDATAZ monolayers versus experimental results.

An understanding of the interaction between PDA and PDATAZ can be provided by comparing the molecular areas of the mixed monolayer, which is calculated through the additivity rule, with the experimental molecular areas:

$$A_{12} = \chi_1 A_1 + \chi_2 A_2$$

A_1 , A_2 , and A_{12} are the molecular areas of monolayer 1, monolayer 2, and a mixed monolayer of 1 and 2 at certain surface pressures. χ_1 and χ_2 are the molar fractions of the two mixed components. Calculation of the 1/1 and 4/1 mixed PDA/PDATAZ monolayer (Figure 4) has indicated that the mixed monolayer does not follow the above additivity rule. The experimental molecular areas in both cases are larger than the calculated values at all different surface pressures. The mixing of the two components caused an expansion of the mixed monolayer.

Photopolymerization Studies at the Air–Water Interface. The photopolymerization of these monolayers at the air–water interface was studied by in-situ UV–vis

absorption spectroscopy. All the monolayers for photopolymerization were compressed to a surface pressure of 30–32 mN/m (except for PDA, which was overcompressed due to its instability), and then irradiated at 254 nm for different periods of time. The UV–vis absorption spectra of PDATAZ in the three subphases (pure water, 10 mM BA, and 10 mM CA) are shown in Figure 5, along with the spectrum of polymerized PDA monolayer on the water subphase for comparison.

There is a distinct difference in the absorption spectra between the polymerized PDA and PDATAZ on the pure water subphase. The absorption spectra obtained from the pure PDA monolayer are similar to the reported results.^{9b,c,e,f,m} From the beginning of irradiation, the polymerized PDA monolayer shows a maximum absorbance at 650 nm, the so-called blue film. Upon increasing the irradiation time (e.g., 200 s), the intensity of the blue form absorption band first increased and then decreased quickly until finally disappeared. At the meantime, another absorption band at 540 nm, the so-called red film, appeared and the intensity kept increasing with prolonged irradiation time. Irradiation of the PDATAZ monolayer for short times also exhibited a typical blue form absorption band, with a maximum absorbance at 620 nm and a sideband at 570 nm. Increasing the irradiation time up to 1000 s increased the intensity of the absorption at 540 nm, while the blue form absorption band still remained. The absorption band of PDATAZ is slightly broader compared to that of PDA. In general, it seems PDA and PDATAZ show the same propensity in their chromatic behavior, although it took much longer for the PDATAZ to shift from the blue to the red form than PDA does. The maximum absorbance of PDATAZ on different subphases are all approximately 0.005 au, which is in good accordance with the reported data on polydiacetylene monolayers, between 0.005 and 0.01 au.^{9b}

There are also obvious differences between the photopolymerization of PDATAZ on the BA, CA, and pure water subphases. On the 10 mM BA subphase, with increasing irradiation time, the maximum absorption did not shift much, remaining at the blue (620 nm) and purple (570 nm) forms. Even after 1200 s irradiation, no obvious absorption band from the red form was evident, only the intensity of the absorption band of the purple form is slightly higher than that of the blue form. The PDATAZ behaved similarly on the CA subphase. No red form absorption band was observed after 1000 s irradiation. Even to the naked eye, the polymerized PDATAZ monolayers on BA and CA subphases exhibited a blue color while the PDATAZ monolayer on the pure water subphase showed up as a slight purple color film.

The photopolymerization of mixed PDA/PDATAZ monolayers in different ratios on the pure water subphase are presented in Figure 6. A striking feature was found that the 1/1, 4/1, and 10/1 ratios of PDA/PDATAZ mixed monolayers only gave a red form absorption band from the beginning of the irradiation. No blue form absorption was observed at any period of irradiation times. For the 1/4 mixture of PDA/PDATAZ, the blue form absorption band is barely visible, the maximum absorption is predominantly the red form. The photopolymerization of the 20/1 ratio of PDA/PDATAZ is similar to that of pure PDA. First a blue absorption band appeared, with prolonged irradiation time, the film turns to red. In contrast, the absorption spectra of 1/10 PDA/PDATAZ looked more or less like the pure PDATAZ. The polymerized monolayer slowly turns from blue to red upon continuous irradiation.

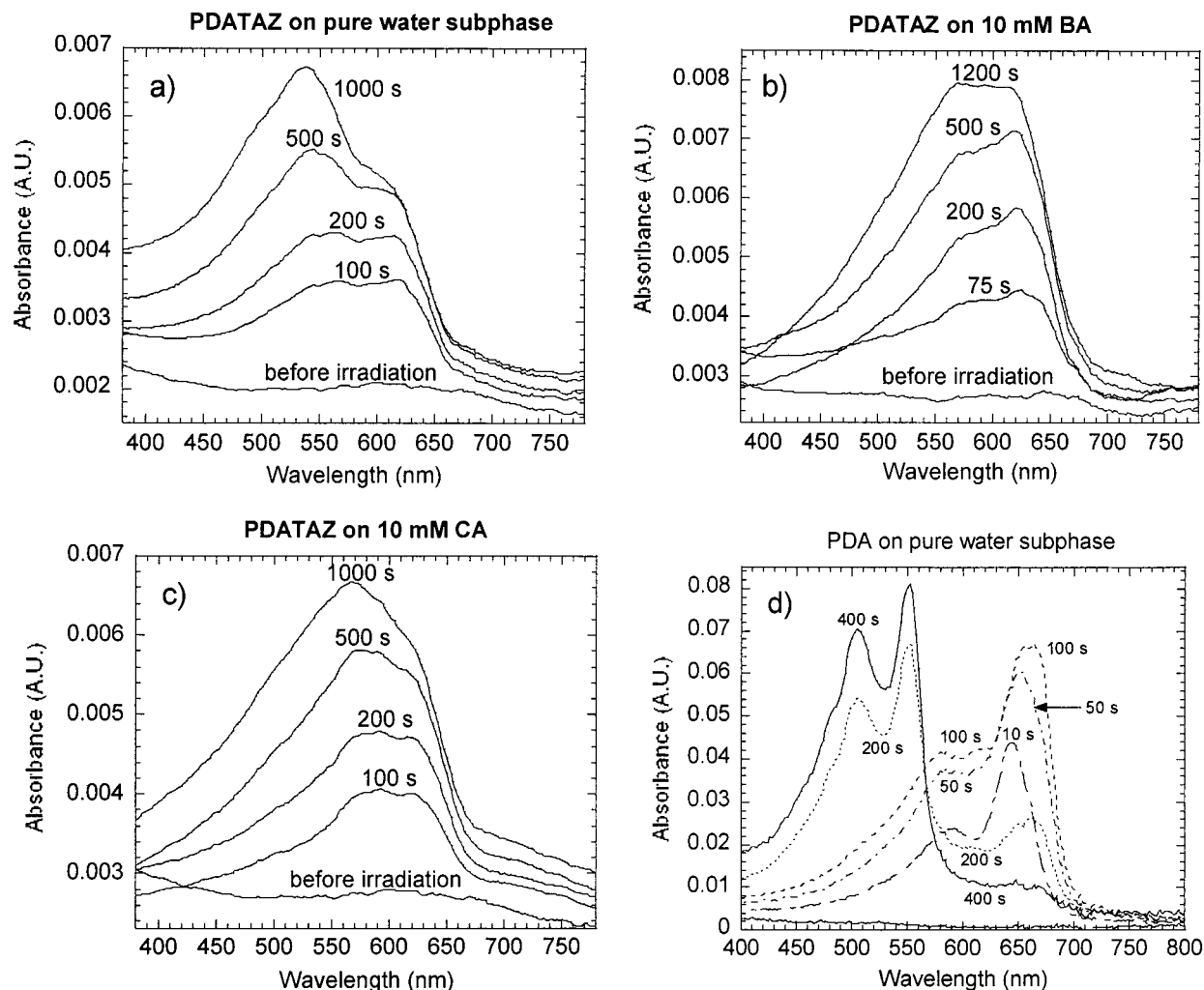


Figure 5. UV-vis absorption spectra of polymerized PDA and PDATAZ monolayers on different subphases: (a) PDATAZ on pure water; (b) PDATAZ on 10 mM BA; (c) PDATAZ on 10 mM CA; (d) PDA on pure water.

Thermochromatic Studies in the Solid State. The color transition for PDA polymer solids was observed around 55 °C, in agreement with the reported results on the PDA Langmuir-Blodgett films and single crystals.^{9e} Upon cooling, the polymer quickly returned to the blue form. Heating the sample above 70 °C resulted in an irreversible color change of the sample from the blue to red form. For the PDATAZ solid sample, when heated to 60–65 °C, the reversible color transition is observed. After increasing the temperature to 150 °C, this polymerized sample still slowly returned to its original blue form upon cooling (about 5 min). Heating to 200 °C causes an irreversible color change. Interestingly, for the 1/1 PDATAZ-BA assembly, the color transition is also observed at 60–65 °C, just as for the pure PDATAZ. However, after heating to 150 °C, the sample returns to the original blue form much more rapidly than the unassembled PDATAZ (ca. 10 s) when cooled. Increasing the temperature to ca. 180 °C turned the heated red sample to dark brown within seconds, the color continued to deepen upon further heating, until it remained as an almost black solid at 200 °C. This black solid began to melt at ca. 300 °C.

Discussion

Although numerous and wide ranging works have been published on the study of polydiacetylenes, there is still a lack of an appropriate and clear model to explain the

chromatic behavior of these polymers. Three chromatic features of polydiacetylenes have generally been observed: (1) One of the most commonly observed features is the reversible and irreversible chromatic change between blue and red forms under external perturbation, such as thermal, mechanical and solvation.^{9,12,15,16} (2) Continuous irradiation can cause polydiacetylenes to change from the blue to the red form.^{9c,f} (3) The blue or red form polydiacetylene appears to be related to the polar headgroup structure, organization, and the molecular packing of the monomers.^{11c} For polydiacetylene Langmuir and Langmuir-Blodgett films, subphases with different pH values or with the addition of salts also effect the chromatic properties of the films.^{9f} In addition, other chromatic properties have also been observed, such as the existence of purple, yellow, and bluish-green forms, although they are less common than the blue and red forms.

At the present time, the widely accepted model to explain the chromatic properties of polydiacetylenes is based on the difference in the effective delocalization length of the π -electron.¹⁹ That is, the red form is thought to have a shorter effective length of π -electron delocalization than the blue form, as indicated from the wavelength of the maximum absorption peaks at 540 and 640 nm. Further more, the effective delocalization length of the π -electrons

(19) Eckhardt, H.; Boudreaux, D. S.; Chance, R. R. *J. Chem. Phys.* **1986**, *85*, 4116–4119.

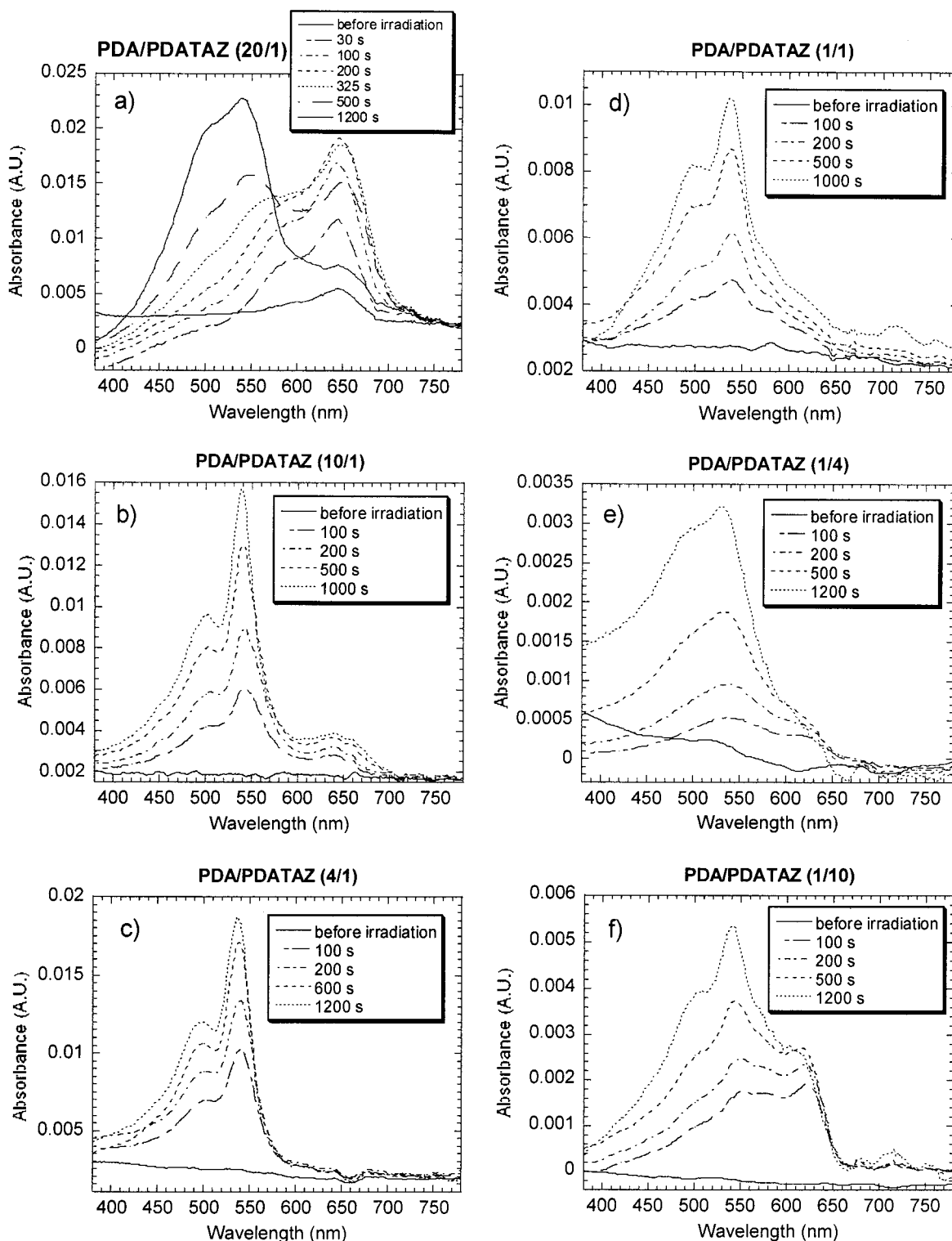


Figure 6. UV-vis absorption spectra of polymerized PDA/PDATAZ mixed monolayers on the pure water subphase in different ratio: (a) 20/1; (b) 10/1; (c) 4/1; (d) 1/1; (e) 1/4; (f) 1/10.

is directly related to the conformations of side chains.²⁰ The red form polydiacetylene is believed to have a disordered side chain conformation and the blue form polydiacetylene has an ordered side chain conformation, as illustrated in Figure 7.^{9e,i}

However, more and more experimental results show that the side chains of red form polydiacetylenes are also in an ordered conformation. For example,^{9q} it was found

that the infrared spectral features for the red form of a polydiacetylene Langmuir-Blodgett film was almost the same as that for the blue form and the broadening of the vibrational bands in the red form was not discernible. Instead, electron diffraction (ED) studies revealed that the difference in the spectroscopic properties (exciton energy levels) between blue and red forms of polydiacetylene is attributed to their molecular packing; that is, the stacking manner or the orientation of the main chain. In both states, the side chains of the polydiacetylenes remain

(20) Tomioka, Y.; Tanaka, N.; Imazeki, S. *J. Chem. Phys.* **1989**, *91*, 5694-5700.

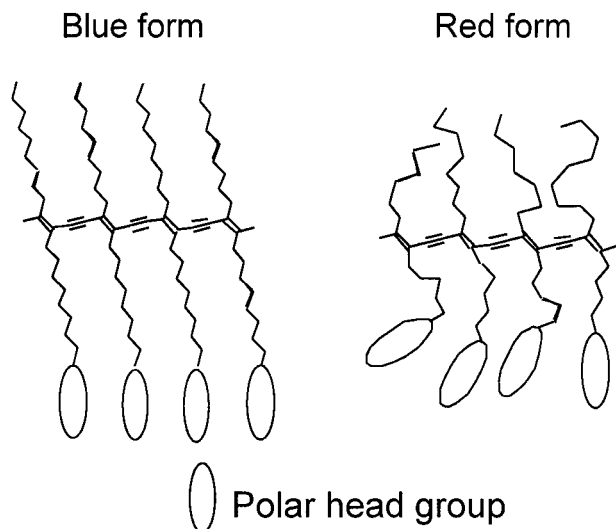


Figure 7. Illustration of the “side chain disorder” model to explain the chromatic property of polydiacetylenes.

in an ordered conformation. In another report,⁹⁰ both FT-IR and atomic force microscopy (AFM) studies of a mixed PDA and sugar-modified PDA Langmuir–Blodgett film also did not show any evidence of disordering of the pendent side chains when the film changed from the blue to the red form. Instead, it appears that the side chains actually become more ordered in the red phase and assume a nearly perfect hexagonal packing.

During our effort to seek a mechanism that can explain all these controversies, the analysis of the chromatic properties of PDATAZ monolayer on different subphases and PDA/PDATAZ mixed monolayers described have brought up some very implicative clues. First, it was unambiguously demonstrated that the addition of complementary components into the subphase has determinant effects on the photopolymerization and the chromatic properties of the resulting polydiacetylenes. As known from the previous studies,^{3,4} TAZ amphiphiles can form a rigid 1:1 linear hydrogen bonding network at the air–water interface with the complementary components from the subphase. It is a quite reasonable assumption that PDATAZ also forms a linear hydrogen bonding network with BA or CA, as shown in Figure 1. Our recent polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS) study at the air–water interface showed that the hydrogen bonding network between TAZ amphiphiles and complementary components BA is so rigid that the NH_2 deformation absorption band from the TAZ moiety is totally absent on a 1 mM BA subphase.²¹

In this linear hydrogen bonding network, one immediately sees that restricting the movement of the triaminotriazine polar headgroup also restricts the motion of the diacetylene side chains connected to the polar headgroups. The side chains are not able to move in any direction and must be in an ordered conformation. The polyenyne backbone maintains an extended chainlike shape, leading to an efficient π -electron conjugation, and the polymer absorbs in the red region to give a blue form absorption band.

However, the above analysis did not automatically bring the conclusion that the side chains are disordered in the

red form polydiacetylenes. In contrast, the photopolymerization studies on mixed PDA/PDATAZ monolayers completely disagree with this conclusion. As shown in the Results, the most striking feature of the absorption spectra of the mixture is that the 1/4, 1/1, 4/1, and 10/1 ratio of PDA/PDATAZ only gave a red form absorption band upon polymerization, no blue form absorption band was observed. Two remarks can be made from these observations. First, while all these irradiated films are in a solid phase or liquid condensed phase, there is no reason to believe that the side chains on these red form polydiacetylenes are in a disordered state or entangled with each other. Second, the total absence of blue form absorption bands during the irradiation suggests that the two components are at least quite miscible, instead of forming individual domains at the air–water interface, because, if PDA or PDATAZ does form separated domains, the chromatic behavior of a single component should be observed. That means blue form absorption bands either from pure PDA or pure PDATAZ should appear within short period of irradiation.

To explain the chromatic behavior of these mixed monolayers, only one most likely possibility is left: the packing manner between the two components PDA and PDATAZ in mixed monolayers. When in a solid or liquid condensed phase, both PDATAZ or PDA can be aligned coplanarly into a straight line, as illustrated in Figure 8a,b. As a consequence, the diacetylene groups are also aligned in a straight line. The polymerization of these monolayers results linear chainlike polyenyne backbone and blue form polydiacetylene films. However, when the two different amphiphiles are mixed together, the situation is more complicated. To obtain maximum stabilization, the two components are most likely packed in a staggered manner as illustrated in Figure 8c. The slight expansion of the mixed monolayer, as described earlier (Figure 4), can be regarded as experimental evidence of this staggered packing manner. In this noncoplanar molecular packing, the diacetylene groups from PDA will be polymerized with the nearby diacetylene groups from PDATAZ; however, the so-formed polyenyne backbone is not in an extended chainlike conformation: it is a “zigzag” structure as presented. With such a highly twisted polyenyne backbone, the required geometry for an effective π -electron conjugation is interrupted and this results in a red form polymer.

Since we have concluded that the two components are at least quite miscible, it can be assumed that in the 1/1 PDA/PDATAZ mixed monolayer, on average, one PDA molecule is interrupted by one PDATAZ molecule; in the 4/1 ratio mixture, every fourth PDA molecule is interrupted by one PDATAZ molecule, and in the 10/1 ratio mixture, every tenth PDA molecule is interrupted by one PDATAZ molecule. All these interruptions force the one-dimensional propagation of the polymer chains to change their direction to result in zigzag polymer backbones. Since the 10/1 ratio mixed monolayer of PDA/PDATAZ still only shows a red form absorption band, we may estimate that the blue PDA polymer film has a polyenyne backbone at least ten enyne units long. For the 20/1 ratio PDA/PDATAZ mixture, twenty PDA molecules can be positioned nearly coplanarly before interruption by a PDATAZ molecule. The polymerization of twenty diacetylene groups from PDA is long enough to allow the effective π -electron conjugation to give a blue form absorption band, which eventually becomes red upon further irradiation. As to the 1/4 ratio PDA/PDATAZ mixture, four PDATAZ molecules interrupted by one PDA molecule, the photopolymerization of the eight diacetylene alkyl chains on the four PDATAZ is not long enough to exhibit an obvious blue form absorption

(21) Huo, Q.; Dziri, L.; Desbat, B.; Russell, K. C.; Leblanc, R. M. unpublished results. The NH_2 deformation absorption band of the triaminotriazine moiety, which originally appeared at 1716 cm^{-1} on the pure water subphase, completely disappeared with the addition of barbituric acid into the aqueous subphase, while new peaks attributed to barbituric acid vibrations appeared.

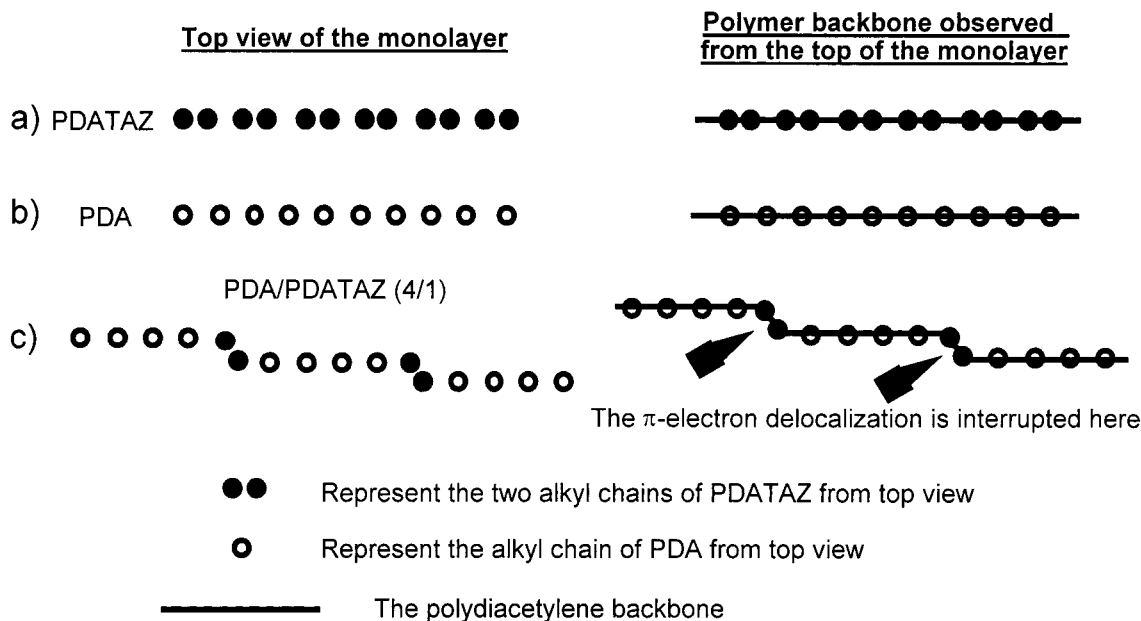


Figure 8. Illustration of the effect of coplanar or noncoplanar packing of pure PDA, pure PDATAZ, and mixed PDA/PDATAZ monolayers on their photopolymerization and chromatic properties.

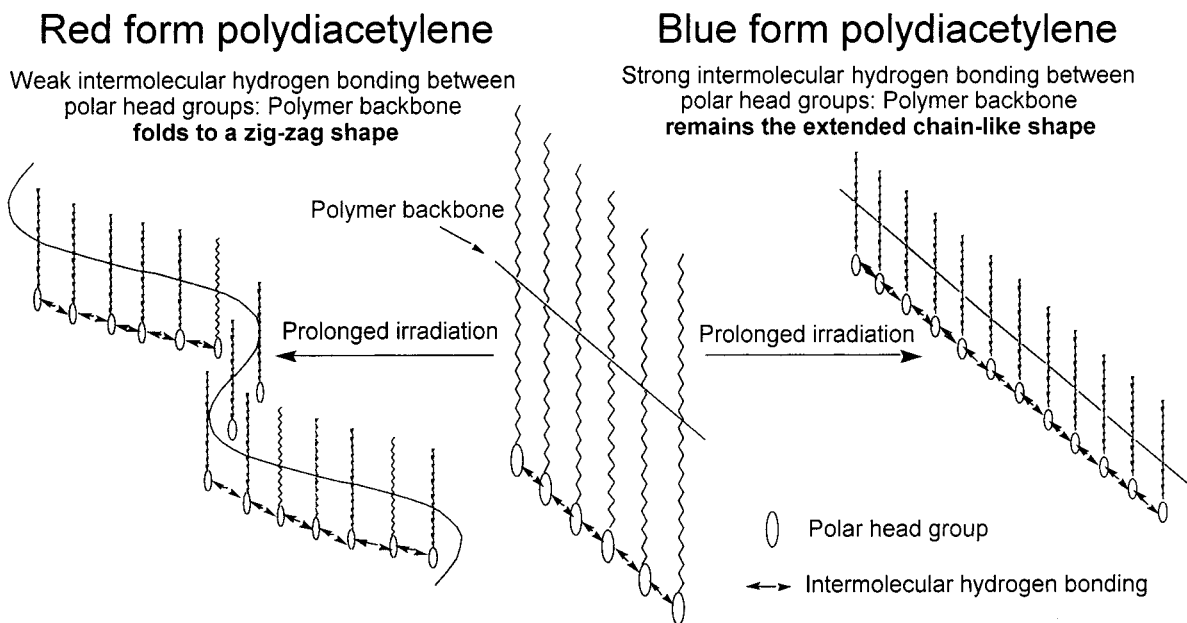


Figure 9. "Self-folding" model of the polymer backbone to explain the chromatic properties of polydiacetylene films upon prolonged UV irradiation.

band (eight enyne units). Continuous irradiation only results in a relatively weak red form absorption band (absorbance 0.003 au, lower than the absorbance of other mixed monolayers). For the 1/10 mixture of PDA/PDATAZ, because PDATAZ is the major component, there are total twenty diacetylene groups in ten PDATAZ molecules, the photopolymerization exhibits a behavior similar to that of pure PDATAZ, first giving a blue form absorption band and then the maximum absorption wavelength slowly shifting to the red form.

Up to this point, one will find the chromatic change of the pure PDA monolayer from the blue to red form upon prolonged polymerization can be easily explained by the zigzag structure of the polymer backbone. Before irradiation, the hydrophobic chains of PDA in the monolayer are organized in the solid-condensed phase. Within a short irradiation time, the length of the polyene chain is still relatively short. The polyene backbone remains as an

extended chainlike shape and achieves efficient π -electron delocalization to result in a blue form absorption band. With increased irradiation time, the polymer length is increased, and the linear polyene chain starts to "self-fold" to a "zigzag" shape, as shown in Figure 9 to obtain a conformation with higher entropy. It is well-known that when a polymer reaches certain lengths, the polymeric main chains tend to adopt folded conformations, due to the free rotation of the single bonds in the polymer main chains.²² Since the polyene backbone also contains numerous single bonds, there is enough reason to believe that the free rotation of these single bonds is the origin of the conformational and therefore the chromatic changes of the polymer backbones.

(22) (a) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953; Chapter X. (b) Bueche, F. *Physical Properties of Polymers*; Interscience Publishers: New York, 1962; Chapter 1.

This process of "self-folding" of a polymer main chain certainly requires the free movement of the side chains connected to the polymer main chain. If there are any strong intermolecular interactions existing between the polar headgroups on the side chains, it will be difficult for this process to take place. For the PDATAZ-BA or PDATAZ-CA monolayers, the formation of the strong linear hydrogen bonding network severely restricts the movement of the polar headgroup and side chains, the "self-folding" of the polymer main chain is significantly inhibited, and the polymer backbone remains in a straight line, leading to efficient π -electron delocalization (Figure 9). Even for PDATAZ on the pure water subphase, as established in our previous work, a noncomplementary hydrogen bonding network is formed between TAZ headgroups.⁴ Even though it is not a completely complementary hydrogen bonding network, the hydrogen bonding is still stronger than the hydrogen bonding formed between the carboxylic groups from PDA. This explains why it takes much longer irradiation for PDATAZ to become a red film than PDA does.

During the self-folding of the polymeric backbone, the alkyl side chains remain in the ordered conformation, only their packing mode at folding points is slightly changed, as illustrated. This explains perfectly why, in recent FT-IR spectroscopy and AFM studies,^{90,q} no obvious differences were observed for the conformation of side chains between the blue and red polymer forms. There are also many other experimental results that strongly support the existence of a zigzag polymeric backbone mechanism. For example, it has been found that the self-assembled monolayers of diacetylene compounds on gold substrates, which are attached through covalent thiol bonds, only exhibit as a blue form film even upon prolonged irradiation.¹⁰ Because the side chains of the polydiacetylene are fixed on the substrate through covalent bonding, the polymer backbone was not able to self-fold. The zigzag structure of red form polydiacetylenes can also explain the chromatic properties of an amino acid-modified PDA liposomes.^{11c} The change of the pH of the water subphase causes the ionization or deionization of the amino acid headgroups. As a result of repulsive Coulombic interactions, the headgroups rearrange themselves to a noncoplanar packing mode to accommodate the new charge distribution. This noncoplanar packing mode results in a zigzag polymer backbone. The polymerized liposomes undergo a color change from blue to red under these conditions.

An understanding of the molecular mechanisms underlying the optical properties of polydiacetylenes has a significant importance in the further application of these polymers. It is commonly accepted that the nonlinear optical properties of polydiacetylenes are introduced by the π -electron delocalization along the one-dimensional polymer backbones. The higher the degree of the conjugation, the larger the nonlinear optical susceptibility.^{6,13} Because self-assembly of PDATAZ and BA or CA can remain as the blue form upon prolonged irradiation time, these supermolecules may become promising candidates for further application investigations as nonlinear optical devices and materials.

The thermochromic behaviors of PDA, PDATAZ, and its assembly with BA in the solid state also revealed the strength and power of hydrogen bonding on the control of material properties. The thermochromic studies of polymerized PDA Langmuir-Blodgett films^{9e} show that the red form absorption band starts to appear at a temperature as low as 50 °C, significantly lower than the melting point of PDA monomer (62–63 °C). Below the melting point, it is very unlikely that the side chains will change to a very disordered conformation. The reversible color transition is most likely caused by the slight folding of the polymeric backbone. The side chains remain in an ordered conformation. With increased temperatures, the polymer chain is significantly folded, and the conformation of the side chains are completely altered, becoming highly disordered or entangled. Even after cooling, the disordered polymer is not able to return to its original extended chainlike conformation; an irreversible color change is observed. If strong intermolecular interactions exist between the polar headgroups of the polymer, one can expect the irreversible color change to occur at a higher temperature than for polymers lacking such interactions. Indeed, while polymerized PDA undergoes irreversible color change at a temperature as low as 70 °C, both PDA and PDATAZ-BA self-assembly can still undergo reversible color transition at a temperature as high as 150 °C. The hydrogen bonding network might be temporarily disrupted during the heating; however, after cooling, the network structure is restored swiftly, leading to the original linear chainlike polydiacetylene backbone.

One noteworthy point regarding the solid state photopolymerization should be addressed. The photopolymerization and the thermochromic examinations of PDATAZ and the PDATAZ-BA assembly suggest that the PDATAZ forms a "linear tape" assembly with BA in the solid state. This result is in contrast to Whitesides' studies on hydrogen bonding self-assemblies.² It was concluded that with bulky substituents, TAZ molecules incline to assemble with BA or CA in polymorphic structures such as crinkle tapes or rosettes, in addition to linear tapes. However, it seems that all the amphiphilic hydrogen bonding complementary components only form extended linear tape hydrogen bonding networks at the air-water interface, polar isotropic media such as water, or multilayer membranes. According to Kunitake's explanation,²³ the amphiphilicity of the hydrogen bonding components is the driving force behind the formation of these linear tape supramolecular self-assemblies. The van de Waals interaction between the hydrophobic long tails may compensate for the steric hindrance of the substituents on the hydrogen bonding components. In other words, the enthalpic advantage during the integration process compensates the entropic disadvantages.

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(23) Kimizuka, N.; Kawasaki, T.; Hirata, K.; Kunitake, T. *J. Am. Chem. Soc.* **1998**, *120*, 4094–4104.