Rational Design of Conjugated Polymer Supramolecules with Tunable Colorimetric Responses

By *Dong June Ahn, Sumi Lee,* and *Jong-Man Kim**

Polydiacetylenes (PDAs), a family of highly π-conjugated polymers, have unique characteristics associated with their ability to self-assemble. Disruption of the extensively delocalized enyne backbones of molecularly ordered PDA sidechains induces a blue-to-red color change, which has been elegantly applied in the design of chemosensors. Recently, colorimetrically reversible PDAs have received significant attention, not only to gain a better understanding of the fundamentals of PDA chromism, but also to develop methodologies to overcome limitations associated with their colorimetrically irreversible counterparts. In this article, recent progress made in the field of colorimetrically tunable (reversible, stable, or sensitive) PDAs is described. Major emphasis is given to rational design strategies developed in our group. Relevant mechanistic investigations, a diagnostic method to test colorimetric reversibility, as well as future challenges in this area will be also discussed.

1. Introduction

Conjugated polymers have been extensively investigated as novel functional materials owing to their intriguing optical and electrical properties associated with extensively delocalized π-electron networks and intrinsic conformational restrictions.[1–5] Especially interesting are stimulus-induced changes that take place in the electronic absorption and emission properties of these substances, which have been elegantly applied to the design of efficient chemosensors.[6–17] Thus, a variety of conjugated polymers have been constructed which undergo color and fluorescence transitions upon environmental perturbation.

Among the conjugated polymers reported to date, polydiacetylenes (PDAs) are unique in several respects.[18–45] First, these polymers can be prepared from supramolecularly assembled crystalline or semicrystalline states of diacetylene (DA) monomers. Conventional solution-based chemical approaches typically employed for the preparation of conjugated polymers do not yield PDAs efficiently. Second, PDAs are produced by UV or γ-irradiation of self-assembled DAs without the need for chemical initiators or catalysts (Scheme 1). Thus, the resulting polymers are not contaminated with unwanted by-products. Third, PDAs are readily prepared in aqueous solution in the form of nanostructured liposomes, vesicles and wires, properties that enable them to be employed as matrices for biosensing. Finally, nanostructured PDAs undergo a blue-to-red color change in response to heat (thermochromism),[23,46,47] organic solvents (solvatochromism),[48–52] mechanical stress (mechanochromism),[53–56] and ligand-receptor interactions (affinochromism).[57–69]

The majority of PDA-based chemosensors, reported thus far, function in an irreversible fashion. Accordingly, the blue-to-red color change that takes place when an external stimulus is applied is not reversed when the external stimulus is removed. PDA systems displaying colorimetric reversibility, especially in aqueous solution, are exceptionally rare. During the course of investigations aimed at developing PDA-based chemosensors[18,49] and colorimetrically reversible PDA supramolecules,[57,70,71] we found that strong headgroup interactions in the PDAs are required in order to bring about complete colorimetric reversibility during repeated heating–cooling cycles. In addition, we observed that strong headgroup interactions make the PDA supramolecules more stable to thermal stimulation.[72] In contrast, colorimetrically sensitive polymers are obtained when DA monomers, having weak headgroup interactions, are transformed to PDAs.[73] Thus, we are now able to control not only the colorimetric reversibility but also the colorimetric temperature window of PDA sensor systems by manipulating the headgroup interactions.

In this Feature Article, an overview is presented of recent achievements in studies of PDA systems that display reversible thermochromism and extreme colorimetric stability. Major emphasis is given to investigations we have conducted with these systems. Mechanistic investigations of PDA thermochromism using in-situ FT-IR and electronic absorption spectroscopic analysis, a diagnostic method for differentiation of the colorimetric reversibility, and future challenges in this area are also described.

2. Chromisms of Polydiacetylene Supramolecules

2.1. Thermochromism

One of the fascinating features of PDAs is the brilliant blue-to-red color transition that takes place upon stimulation, such as heat,

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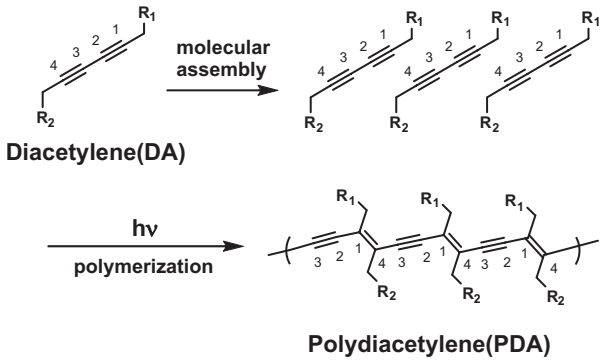
solvent, mechanical stress, and specific molecular recognition. Among the various chromic transitions of PDAs, the most extensively explored properties are thermally induced color transitions.[23,46,47] For example, heating a suspension containing PDA vesicles causes a blue-to-red color change, as displayed in Figure 1A. The PDA thermochromism is not limited to dispersed



Scheme 1. Schematic representation of the polymerization of self-assembled diacetylenes promoted by irradiation with UV light.

suspensions since it is also observed with casted thin films,[74] Langmuir–Blodgett (LB) or Langmuir–Schaefer films,[71] as well as single crystals[46] and solid powders.[47]

Numerous investigations have been carried out to gain a better understanding of the origin of PDA thermochromism.[75–79] Despite this intense effort, the exact mechanism of the blue-to-red color transition is still not fully understood. The results of recent studies with urethane-substituted PDAs, however, strongly suggest that the release of mechanical strain, developed on the side chains during polymerization, is the main factor responsible for the thermally promoted color transitions.[47] The release of sidechain strain induces a partial distortion of the conjugated p-orbital arrays, leading to a shortening of the effective π-conjugation length. Our recent observations with a carboxyphenylamido-substituted DA monomer, provide further support for this proposal (vide infra).[70]

2.2. Solvatochromism

The molecularly ordered states of supramolecular PDAs can be influenced also by the presence of organic solvents. PDAs with

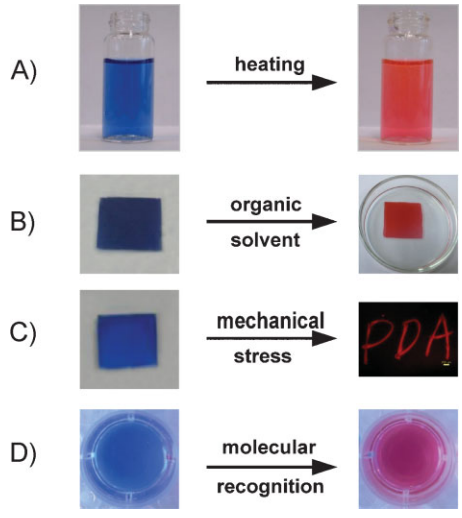


Figure 1. Examples of PDA chromism. A) thermochromism, B) solvatochromism, C) mechanochromism, D) affinochromism.

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alkyl-urethane pendent groups, ether in solution or in the crystalline state, have been exposed to various solvents. Addition of a non-solvent to chloroform solutions of urethane derived PDAs causes a color change from yellow-to-blue or -red, depending on the nature of sidechain substituents.[48] Exposure of single crystals of the PDA derived from bis(ethylurethane)-5,7-dodecadiybe-1,12-diol (ETDC) to boiling chlorobenzene results in the significant blue shift in the near-normal incidence reflection spectra.[51] The color change of the crystals is attributed to the loss of the unreacted monomers and oligomers, which results in an increase in the lattice volume. Thus, reduction of the restriction of a mechanical strain imposed on the polymer sidechains may induce partial distortion of the conjugated p-orbitals, leading to the blue-shift in the reflection spectra.

In Figure 1B are shown fiber mats embedded with PDA molecules before and after incubation in chloroform.[49] The PDA-encapsulated fiber mats were prepared by electrospinning viscous solutions containing DA monomers and matrix polymers. UV irradiation of the electrospun fiber mats causes photopolymerization of DA monomers in the fiber mat and the resultant formation of blue color. The red color developed when these mats are exposed to chloroform is a consequence of solvatochromism, originating from the disruption of the highly ordered lipid assembly promoted by interaction with the organic solvent.

The observation of an organic solvent induced, blue-to-red color transition of PDA embedded electrospun fibers is interesting since it suggests that the colorimetric response might depend on both the nature of the organic solvent and the structure of DA monomer. If so, it would be possible to colorimetrically differentiate organic solvents by using this methodology. In order to probe the feasibility of visual, solvent sensor systems based on this technology, PDA-embedded fiber mats were prepared from different monomers.[49] Interestingly, polymer mats containing polymerized DAs show different colorimetric responses upon exposure to the organic solvents. Thus, the organic solvent-dependent color change property of the PDA-embedded polymer mats allows for a straightforward procedure based on ''color patterns'' to differentiate between several common organic solvents.

2.3. Mechanochromism

Mechanochromism is the phenomenon of color change induced by applying pressure. Materials displaying this property can be utilized in recording or pressure-sensing systems.[80] In Figure 1C is shown a photograph of blue-colored PDA film on a glass substrate (left) and a fluorescence microscopic image obtained after scratching the blue colored film using a syringe needle (right). Scratching of the film imposes shear stress on the PDA film and this promotes a blue-to-red color change. Since red-phase PDAs fluoresce,[81–83] only the scratched areas emit fluorescence.

The mechanochromic properties of PDAs have been observed in both macroscopic and nanometer size systems. Pressure-induced chromism of partially polymerized PDA monolayers prepared from 10,12-heptacosadiynoic acid was reported.[53] Observation of an irreversible chromic transition of a PDA single crystal, induced by mechanical stress was also described.[54] Polyurethane elastomers containing a small fraction of PDA chains in their hard domains were found to undergo color changes from blue to red or yellow during stretching.[55]

More recently, an interesting nanoscale mechanochromism of the PDA trilayer films on solid substrates was reported by Burns and coworkers using tips of scanning probe microscopes.[56] Shear forces between the probe tip and the PDA molecules was observed to induce a blue-to-red color change in the contacted areas that was readily detected by fluorescence monitoring. Previously, it has been suggested that the red-phase PDA is in more disordered state than the blue-phase counterpart.[84] However, observations made with AFM images of the blue- and red-phase PDAs confirm the alkyl chains in red-phase PDAs exist in a more ordered state.[85] The observations made with AFM images, ^{13}C NMR data reported by Tanaka et al.,[86] and theoretical calculations from Tripathy et al.,[78] have led to the suggestion that the shear forces imposed on the PDA film induce sidechain rotation about the conjugated backbone which reduce the effective conjugation length of the polymer.

2.4. Affinochromism

Probably, the most attractive feature of PDAs to be uncovered in recent investigations concerns the novel chromic (color or fluorescence) changes promoted by interactions with biologically, environmentally or chemically interesting target molecules. Since PDA sensors display an observable blue-to-red color change upon exposure to the target molecules, additional procedures that are required in a common enzyme-linked immunosorbant assay (ELISA) system are not necessary. By taking advantage of their label-free function, a variety of colorimetric PDA sensor systems have been developed for monitoring ligand-receptor interactions.[57–69] In Figure 1D is shown the chromic transition induced by interaction of a PDA derived from 10,12-pentacosadiynoic acid (PCDA) with alpha cyclodextrin discovered by our group.[57]

Charych demonstrated that PDAs serve as fascinating sensor matrices for the detection of biologically interesting target molecules.[58] In an exceptionally interesting early experiment, Charych and coworkers prepared a PDA Langmuir–Blodgett (LB) film, functionalized with sialic acid, and showed that the film undergoes a blue-to-red color change when exposed to an influenza virus. PDA films and vesicles, functionalized with carbohydrates, have proven to be effective biosensors for the detection of the influenza virus,[59] cholera toxin,[60] and *E. coli*.[61] PDA vesicles immobilized with probe DNA molecules undergo blue-to-red colorimetric transition upon binding with complementary strands of DNA, enabling them to be used as colorimetric DNA sensors.[62] Very recently, a method for the detection of polymerized chain reaction (PCR)-amplified double stranded DNAs based on ionic interactions was reported.[63]

Colorimetric detection of glucose, based on ligand-induced conformational changes of hexokinase immobilized on a PDA monolayer, represents another elegant application of PDA-based biosensing.[64] A system for selective detection of metal ions, formed by embedding an ionophore into a PDA liposome, also has been reported.[65] A PDA-based enzyme detecting sensor,

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driven by a hydrophilic-to-hydrophobic transformation of an enzyme substrate, has been described recently.[66] In this system, hydrophobic products of enzyme catalyzed reactions of hydrophilic substrates perturb the ordered structures of PDAs, thus causing the color transition. Very recently, colorimetric PDA sensor systems, based on specific antibody–antigen (epitope) interactions, have been developed.[67–69]

3. Colorimetrically Reversible Polydiacetylenes

As described in the introductory section, most PDAs undergo an irreversible color transition. Only a limited number of colorimetrically reversible PDA systems have been reported (vide infra). In light of the significance of reversibly functioning PDAs in terms of multiple usages of sensor materials and as a consequence of the still-puzzling mechanistic features of PDA chromism, the development of PDAs that display reversible color transitions is a very important goal.

3.1. Reversible Thermochromism in Solid State

Early investigations of the reversibility of thermochromism were carried out for the most part with PDA crystals. For instance, Chance and coworkers observed a reversible color transition over the temperature range of 23–130 °C with a PDA crystal prepared from the urethane-substituted DA monomer **1** (Fig. 2).[46] Based on normal incidence reflection spectral data, these workers suggested that a thermally induced structural change takes place transforming the PDA backbone from a polyacetylene to polybutatriene. That an acetylene to butatriene transformation of the PDA backbone taking place in this system was ruled out by the results of solid state ^{13}C NMR experiments. Sandman and coworkers thoroughly investigated phase transition of the **1**-derived PDAs by a solid-state ^{13}C cross-polarization and magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) and demonstrated that the acetylenic ene-yne backbone structures of the polymer remain unchanged during the thermal cycles.[47]

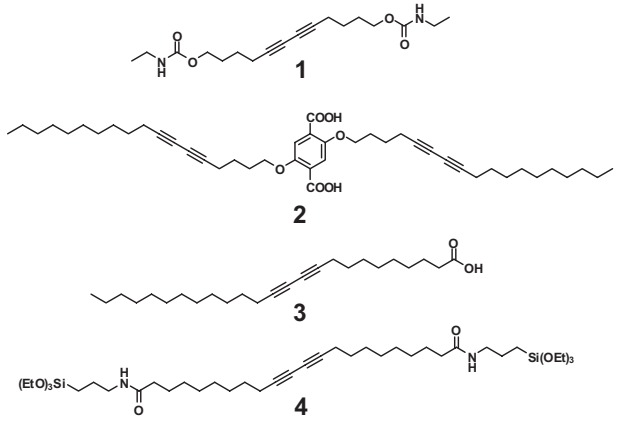

Figure 2. Structures of diacetylene monomers employed to investigate reversible thermochromism.

Recently, Lee and coworkers designed a new and interesting PDA system which participates in reversible thermochromism.[87] A spin-coated polymerized thin film, obtained from the bisdiacetylene-substituted terephthalic acid **2**, was found to show complete colorimetric reversibility during repetitive heating and cooling cycles. The hydrogen-bonding networks formed between the aromatic dicarboxylic acids are presumably responsible for the reversible chromism. Accordingly, extensive hydrogen bonding helps restore the original conformations of the PDA chains after removal of the thermal stress.

In general, supramolecular PDAs derived from 10,12-pentacosadiynoic acid (PCDA) (**3**), are colorimetrically irreversible, independent of whether they are prepared in aqueous solution or in thin films. Reversible thermochromism was achieved, however, when a ''brick and mortar'' structure was created with the diacetylene monomer **3** and poly(vinylpyrrolidone) (PVP).[88] Interestingly, annealing the mixture of **3** and PVP at 65 °C (slightly higher temperature than the melting point of **3** of 63 °C) afforded hierarchly self-assembled PDA/PVP nano-aggregates. The authors suggest that hydrogen bonding between carboxylic acid moieties of **3** and PVP is responsible for the reversible thermochromism. It should be noted that an aqueous suspension of the nano-aggregates also displays a reversible color change. Observation of a reversible color transition with PCDA **3**, molecularly assembled and immobilized on a Ag surface, represents another example of a transformation of an irreversible PDA to reversibly functioning supramolecule.[89]

Very recently, colorimetrically reversible PDA–silica nanocomposites were described.[90,91] A thin polymerized film on a glass slide, prepared from the precursor sol derived from the ethoxysilane-containing diacetylene monomer **4**, was found to show complete colorimetric reversibility. Instead of employing noncovalent hydrogen bonding, the sidechains in this system are covalently connected to the inorganic silica networks in the hybrid structure. It has been suggested that the strong covalent interactions that occurs between PDA sidechains and the inorganic silica frameworks play significant roles in the observed reversible thermochromism. The stable covalent interactions are believed to provide sufficient energy for the PDAs to restore the original chain conformations upon returning to the original low temperature state.

3.2. Reversible Thermochromism in Organic Solvents

The preparation of PDA systems that function in a colorimetrically reversible manner in organic solvents is very challenging. In organic solvents, DA monomers tend to be either completely soluble (polymerization does not occur in this case due to the lack of suitable molecular assemblies) or to aggregate to form solid precipitates (polymerization does occur in some cases). Accordingly, fabrication of well-dissolved and molecularly assembled DA supramolecular structures itself is a very difficult task. Jonas and coworkers discovered that acidic forms of the hydrazide-derived single-chain DA lipid **5** in CH_2Cl_2 produce self-assembled DAs, which subsequently polymerize upon irradiation with UV light to yield a blue colored PDA solution (Scheme 2).[92] It is rather surprising that photopolymerization of **5** takes place in organic solution. In the HCl salt form of

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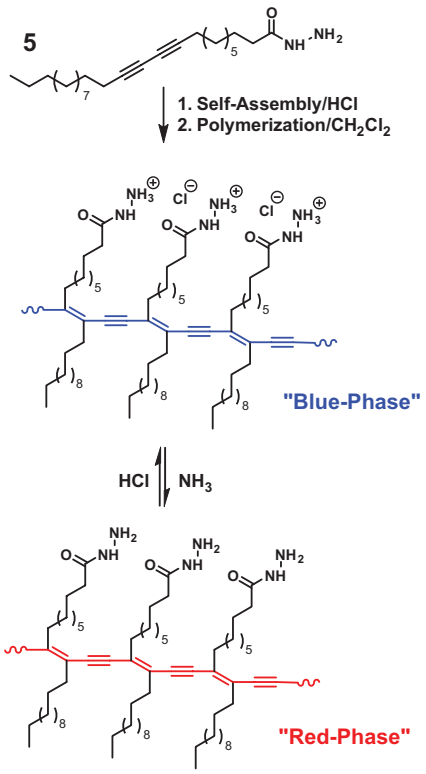
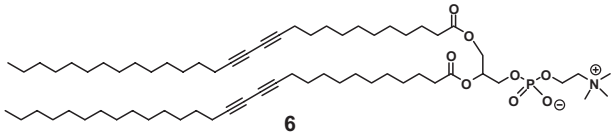


Scheme 2. The structure of the hydrazine-derived diacetylene monomer **5** and a schematic representation of its polymerization in an organic solvent followed by reversible phase transitions of the resulting PDA in the presence of NH_3 or HCl.

5, chloride ions make bridges to the neighboring hydrazide moieties and, as a result, allow for suitable packing of the DA monomers. Moreover, upon addition of NH_3 to the CH_2Cl_2 solution of the PDA a color change from blue to red occurred. Interestingly, the colorimetric transition was reversible in that addition of HCl to the NH_3-treated red-colored CH_2Cl_2 solution resulted in recovery of the original blue color.

3.3. Reversible Thermochromism in Aqueous Solution

Although numerous PDA supramolecules have been prepared in aqueous solution, most of these undergo irreversible color transition upon stimulation. To the best of our knowledge, only one example of a colorimetrically reversible PDA was described prior to our recent efforts in this area. In the earlier work carried out almost two decades ago by Singh and coworkers, an aqueous suspension of the polymerized DA obtained from the bisdiacetylenic phosphorylcholine **6** was found to undergo reversible thermochromism in the range of 10–60 °C.[93]



In the course of recent investigations aimed at the development of PDA-based chemosensors, we found that the PDA supramolecules, derived from the carboxy-substituted DA monomer **7** (Fig. 3), display a completely reversible color transition upon thermal stimulation.[70,71] Thus, heating a suspension containing PDA supramolecules prepared from **7** results in a blue-to-purple color change at 90 °C. Upon cooling, the suspension returns to the original blue color immediately. The colorimetric reversibility of the **7**-derived PDA was further confirmed by visible absorption spectroscopic analysis. When the temperature of the suspension is raised from 25 °C to 90 °C, the absorption maximum of the solution at 640 nm undergoes a gradual blue shift, which plateaus at 580 nm (Fig. 5B). Upon cooling to 25 °C, the absorption maximum shifts back to 640 nm and the original intensity is recovered. The complete, thermally promoted colorimetric reversibility of this system was demonstrated by repeating the thermal cycle without loss of the initial and final respective intensities at 640 and 580 nm, respectively. In addition, when the PDA suspension is subjected to prolonged heating at reflux, the color of the solution becomes pink and the original blue color returns when the solution is cooled to room temperature.

Owing to the fact that the complete thermochromism observed with the PDA supramolecules obtained from **7** is very intriguing, we have systematically investigated the origin of the colorimetric reversibility.[70] Specifically, the effects of 1) amide hydrogen bonding, 2) aromatic interactions, 3) alkyl chain lengths, and 4) carboxylic groups on the reversibility thermochromism have been explored using a variety of diacetylenic lipids (Fig. 3).

In contrast to the **7**-derived PDAs, a suspension of polymer vesicles prepared from **8**, an ester analog of **7**, does not display thermally stimulated colorimetric reversibility. Heating a solution of this PDA from room temperature to 90 °C produces a color change from blue to orange-red and the original blue color does not return completely when the solution is cooled to 25 °C. Heating the suspension from room temperature to 90 °C results in a shift in the absorption maximum from 640 nm to 550 nm where it remains almost unchanged (only partial recovery of the peak at 640 nm) upon cooling the solution to 25 °C. Observations made in studies with polymer vesicles prepared from **8** clearly indicate that the presence of internal hydrogen-bonding amide groups is required in order to obtain a reversible color change upon thermal stimulation. A similar observation was made in solid-state ^{13}C NMR studies of urethane-substituted polydiacetylene powders.[47]

The next systems studied enabled us to probe the effects of the aromatic interactions on colorimetric reversibility. Compared with **7**, the aminobutyric acid **9** has a similar distance between the amide and the terminal carboxylic group but it does not contain a phenyl ring. A comparison of the properties of polymers derived from **7** and **9** give useful information about the effect of structure on colorimetric reversibility. Spectroscopic monitoring and visual observation of polymerized vesicles prepared from **9** demonstrate that the vesicles display only partial colorimetric reversibility. This observation demonstrates the importance of aromatic headgroups. In order to gain more information about the role of the phenyl group, polymerized vesicles prepared from **10**, which has a shorter alkyl chain connecting the headgroup than in **9**, were investigated. The color of a solution of these vesicles changed from blue to orange-red

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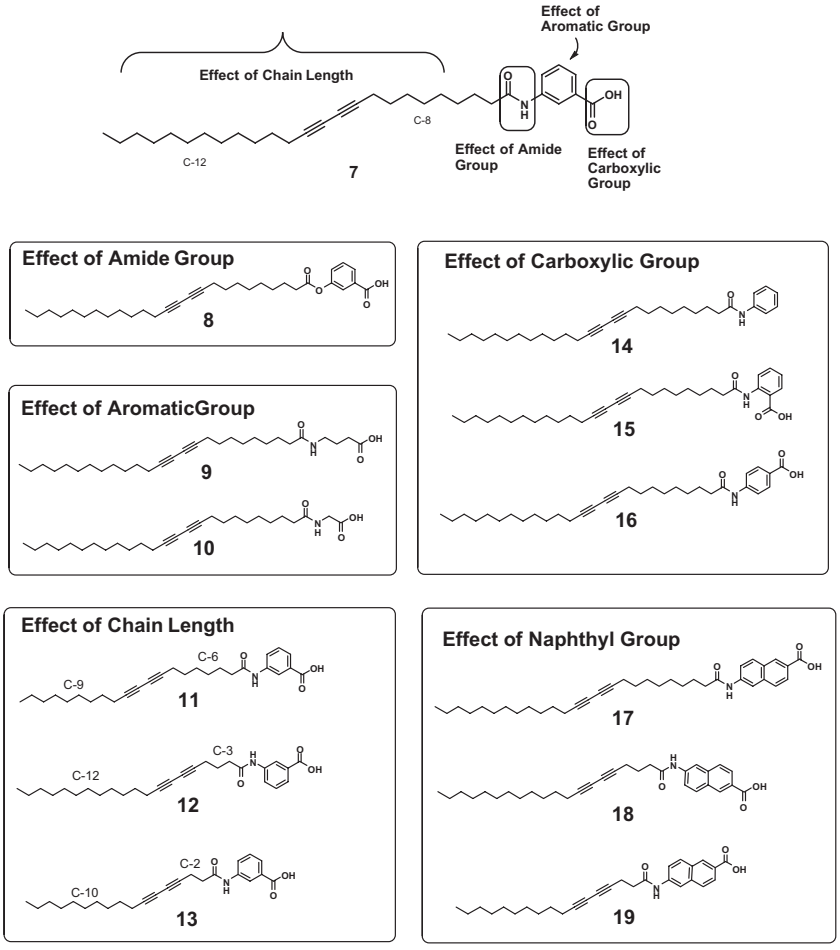

Figure 3. Structures of diacetylene monomers used in investigations of reversible thermochromism in aqueous solution. Reproduced with permission from [70]. Copyright 2005 American Chemical Society.

upon heating and the orange-red color remained unchanged when the solution was cooled to 25 °C.

The effect of hydrophobic carbon chain lengths on the reversible thermochromism was investigated by using PDAs derived from **11**, **12**, and **13**. These three lipids have the same headgroups but shorter alkyl tails than does **7**. Interestingly, the length of the alkyl chain was found to have a negligible effect on the colorimetric reversibility of the resulting polymerized vesicles. Thus, complete reversibility was observed with solutions containing the polymer vesicles made from **11**, **12**, and **13**.

Investigations of the effects of hydrophobic chain length on colorimetric reversibility have led to the important conclusion that colorimetric reversibility can be achieved when strong interactions between headgroups are present, even though the DA monomers have relatively shorter alkyl chains. It is intriguing that the PDA vesicles prepared from **13**, which has only two methylene units between the diacetylene group and the amide headgroup, are stable and blue-colored. The parent diacetylenic lipid, 4,6-heptadecadiynoic acid (HDCDA), which has the same number of methylene units as **13**, was found to form highly unstable polymer vesicles that eventually generate significant amounts of aggregates.

The effect of the terminal carboxylic groups on colorimetric reversibility was probed by using PDA vesicles made from lipid monomers **14**, **15**, and **16**. Among the three, only DA monomer **16** produces stable, blue-colored polymer vesicles which in suspension display complete colorimetric reversibility. The ineffectiveness of vesicle formation with **14** indicates that PDA polymers containing terminal carboxylic acid groups are optimal for further applications. Two important reasons exist for this conclusion. First, the hydrophilic nature of carboxylic groups allows efficient formation of lipid bilayers in aqueous solution. Second, carboxylic acid groups form strong hydrogen bonds with neighboring carboxylic groups. Accordingly, the DA derivative **14**, which lacks a carboxylic acid group, does not form polymerized vesicles in aqueous solution. In addition, the ortho-substituted lipid monomer **15**, undergoes photopolymerization to afford unstable, purple-colored polymer vesicles that immediately aggregate. This result is presumably caused by the preference for intramolecular hydrogen bonding between the amide and ortho-positioned carboxylic groups which blocks interchain hydrogen bonding. Supporting this proposal is the finding that the para-substituted DA lipid **16** generates blue-colored and stable polymer vesicles in aqueous solution that display complete colorimetric reversibility.

The effect of naphthyl groups on colorimetric reversibility was probed by using solutions of polymer vesicles generated from **17**, **18**, and **19**. The three monomers have naphthalene moieties and, as a result, the degree of aromatic interactions is expected to be larger than in polymers made from the phenyl analogs **7**, **12** and **13**. In fact, a solution of polymer vesicles derived **17**, **18**, and **19** all display complete colorimetric reversibility upon thermal stimulation. In addition, it was observed that polymer vesicles prepared from these monomers are much more stable than those derived from the corresponding phenyl analogs. A comparison of the colorimetric properties of PDAs derived from **17** and **19** indicates that the latter PDA, which has a shorter alkyl side chain, is more sensitive in changing color upon a thermal stimulus.

The observations made in studies with the series of structurally related PDAs shown in Figure 3 strongly suggest that cooperative and integrated interactions between amide, aromatic, and carboxylic acid headgroups serve as a necessary condition for achieving thermally promoted colorimetric reversibility of polymerized DA supramolecules.

3.4. Mechanistic Aspects

The mechanism for the blue-to-red color transition of the PDAs has attracted as much attention as its application in the design of

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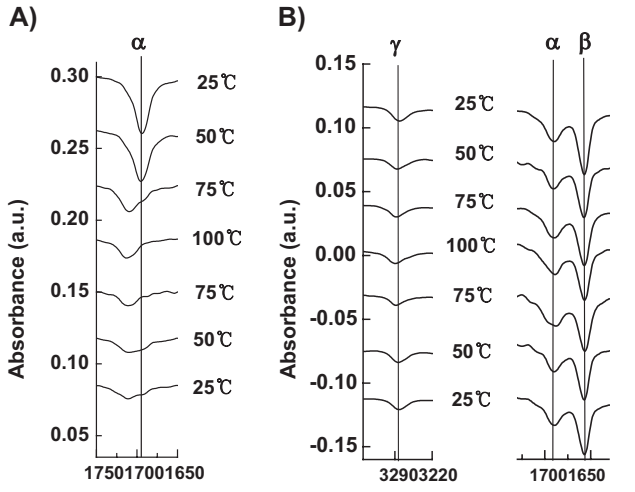

Figure 4. In-situ near-normal external reflection FTIR spectra of LS films of diacetylene monomers **3** (A) and **7** (B) on hydrophobized glasses: α, β stand for carbonyl stretching bands in terminal carboxylic positions and amide positions, respectively and γ stand for the NH stretching band in the amide group. Reproduced with permission from [70]. Copyright 2005 American Chemical Society.

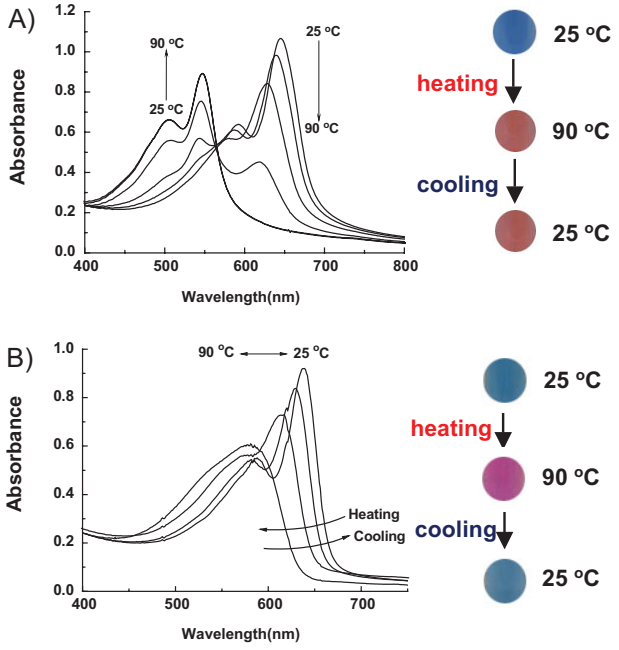

Figure 5. Visible spectroscopic monitoring PDA suspensions prepared from diacetylene monomers **3** (A) and **7** (B) during thermal cycles. Photographs of the suspensions recorded upon heating and cooling processes are also presented.

polymeric chemosensors. A variety of experimental and theoretical techniques have been employed[47,75–79] to gain an understanding of this unique colorimetric transition. Although the exact mechanism for this process is not yet fully understood, observations have been made that suggest that the release of side-chain strain taking place upon stimulation causes rotation about the C–C bonds in PDA backbone. This conformational change perturbs the conjugated p-orbital array and leads to a change in the chromophore responsible for the electronic transition.

In Figure 4 are shown carbonyl stretching bands of in-situ FTIR spectra of Langmuir–Schaefer (LS) films of PDAs prepared from both DA monomer **3** (Fig. 4A), which yields a PDA that displays irreversible thermochromism, and **7** (Fig. 4B), one that gives a PDA with reversible thermochromism.[70] When heated to >75 °C, the hydrogen-bonded carbonyl stretching band of the film from **3** shifts from an initial value of 1694 cm^{-1} to 1712 cm^{-1}, indicating that the strength of the hydrogen bond has decreased. However, upon cooling the sample to 25 °C, the carbonyl stretching band remains at ca. 1711 cm^{-1} showing that the strength of hydrogen-bonding is not recovered in a reversible manner. In contrast, the LS film derived from **7** retains the strength of its hydrogen-bond throughout the heating and cooling cycle as indicated by the absence of a change in the position of the carbonyl stretching band. These findings demonstrate that headgroup hydrogen bonds are not altered throughout the thermal heating–cooling cycle in the case of reversible PDAs. Similarly, when the colorimetrically reversible PDA films prepared from **11**, **16**, and **17** are subjected to the thermal cycle, the peak position and intensity of their hydrogen-bonded carbonyl bands remain nearly constant. The trends noted in the FTIR studies show that strong hydrogen bonding and aromatic interactions, which are retained at high temperature, are essential requirements for the reversibility of thermochromism in PDA supramolecules.

We have also observed interesting phenomena regarding the thermochromic behavior of certain PDA supramolecules. Visible spectra obtained by monitoring solutions containing colorimetrically irreversible PDA vesicles display isosbestic points (or pseudo isosbestic points) in association with their thermally induced blue-to-red color transitions.[94] In contrast, spectroscopic monitoring of color changes taking place upon heating colorimetrically reversible PDAs shows that no isosbestic points are present. Instead gradual blue shifts in the absorption maxima of these substances occur.[95]

In Figure 5A is shown the results of heating of a colorimetrically irreversible PDA solution prepared from DA monomer **3**. As can be seen, heating causes a decrease of the intensity of the absorption band at 640 nm and a simultaneous increase in the absorbance at 550 nm. Interestingly, the heat induced spectral changes are associated with the presence of an isosbestic point at 565 nm. Since PDA vesicles are formed by the self-assembly of diacetylene monomers in aqueous solution, a wide range of vesicle sizes and shapes should be present. Thus, the existence of isosbestic points for the colorimetric transitions of the PCDA-derived PDAs indicates that the individual PDAs respond in a similar manner to thermal stimulation. Different observations were made while monitoring the thermochromic behavior of colorimetrically reversible PDAs. The spectra (Fig. 5B) obtained during heat treatment of a PDA solution prepared from DA monomer **7** does not contain an isosbestic point. Instead, a gradual blue shift of the absorption maximum takes place when the temperature is raised from 25 °C to 90 °C. Upon cooling to 25 °C, the absorption maximum shifts back to 640 nm and the original intensity is recovered. A gradual blue shift of the absorption maximum is observed in visible spectra recorded during heat treatment of

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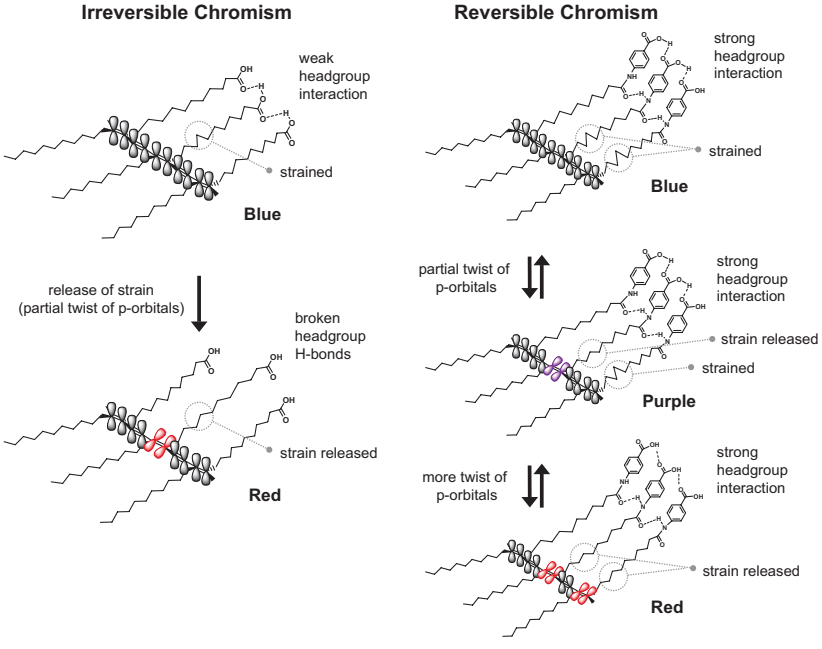
solutions of PDAs, derived from other DA monomers, which display the complete colorimetric reversibility.

The existence of isosbestic or pseudo isosbestic points associated with visible spectral changes induced by heating colorimetrically irreversible PDA systems indicates that the process involves a direct conversion of a blue state to the red state, i.e., without the existence of intermediate states. This observation shows that the purple color that develops when colorimetrically irreversible PDAs are heated is caused by a combination of blue and red PDAs. Also, the gradual shift in the visible maximum, which is observed upon heat treatment of colorimetrically reversible PDAs, shows that the color transitions in these systems are associated with processes taking place through a variety of intermediate states. Thus, a number of near-equal energy states must exist and heating must 1) allow the interconversion between these states to take place and 2) cause a change in the equilibrium constants between these states.

Based on the results arising from the visible spectroscopic monitoring and those coming from the in-situ FTIR experiments, it is possible to propose the mechanisms outlined in Scheme 3 for thermochromism of PDA systems. It is believed that headgroup interactions (hydrogen bonding, aromatic interactions, etc.) play significant roles in governing the molecular orientation of the methylene chains of PDAs, which are formed in a distorted state during the polymerization process. The distortion results in mechanical strain in the PDA backbone. In the case of colorimetrically irreversible PDA systems, exemplified by the PDAs arising from **3**, headgroup interactions are relatively weak. Thus, the release of the mechanical strain upon thermal stimulation results in C-C bond rotation of the polymer backbone and weakening of headgroup hydrogen bonding interactions. Once the mechanical strain developed during polymerization is released and hydrogen bonds are broken, the original molecular orientation cannot be restored by removal of the stimulation (for example cooling to 25 °C). The existence of isosbestic points in spectral changes paralleling the thermal transition indicates that the strain release and hydrogen bond cleavage occurs without the formation of intermediate states. In other words, only blue and red states exist in terms of π-conjugated chromophores for the colorimetrically irreversible PDAs and the disruption of π-conjugation occurs abruptly.

In contrast, transitions between the blue and red states of colorimetrically reversible PDAs take place by a different pathway. In the reversible PDAs, headgroup interactions are strong and they are maintained through out the course of thermal stimulation. In addition, the gradual blue shift occurring in the absorption maxima upon thermal stimulation of reversible PDAs shows that several intermediate states exist with gradually decreasing effective conjugation lengths. Thus, in these cases the release of the mechanical strain in the side chains causes only partial twisting of the conjugated p-orbital arrays to generate sequentially a number of intermediate states. With time, the chromophores become increasingly distorted which results in a decrease in conjugation until the red state PDA is formed. Since strong headgroup interactions present in the starting blue states of reversible PDAs still exist in their red states, the energy differences between these states are small and the energy barriers for reformation of the blue states are low. Thus, the original blue state conformation can be restored once the thermal stress is removed. In other word, the gradual blue shift occurring in the absorption maxima upon thermal stimulation of reversible PDAs shows that several intermediate states exist with gradually decreasing effective conjugation lengths.



Scheme 3. Schematic representations of the mechanisms of chromic responses of irreversible and reversible PDAs.

3.5. Colorimetrically Reversible PDAs from A Bridged Diacetylene Monomer

Recently, we discovered another intriguing PDA system that displays complete colorimetric reversibility in an aqueous suspension.[96] The bisdiacetylene **20**, shown in Figure 6, contains several unique features including a hydrophilic ethylene glycol moiety, two internal amide groups, two phenyl groups, and two DA units. The hydrophilic nature of the ethylene glycol group should favor interaction with water molecules and force the two DA-containing hydrophobic alkyl chains to be located closer together. In addition, the amide groups of **20** are expected to interact with one another by hydrogen bonding either in an intramolecular or in intermolecular fashion. The aromatic interaction between the two phenyl groups could serve as an additional attractive force to bring the diacetylenic units close together.

Monitoring the thermochromism of PDAs derived from **20** by using visible absorption spectroscopy reveals that a completely reversible color transition takes place (Fig. 6). At 20 °C, the PDA solution has the typical blue color

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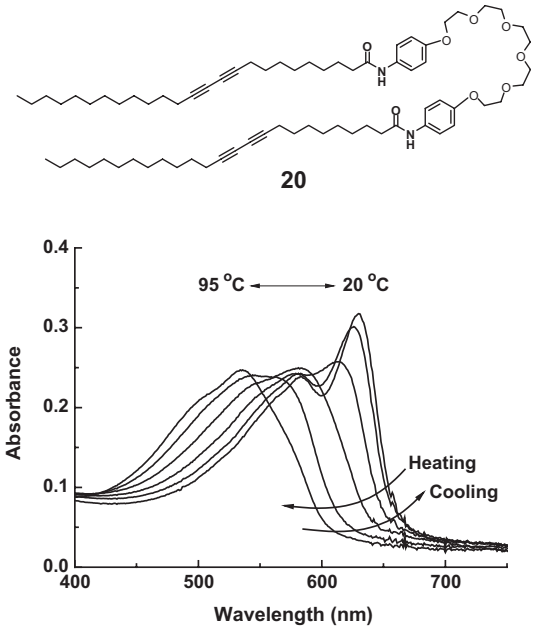


Figure 6. Structure of the bisdiacetylene **20** and visible spectroscopic monitoring of a PDA suspension prepared from **20** upon heating and cooling. Reproduced with permission from [94]. Copyright 2007 The Chemical Society of Japan.

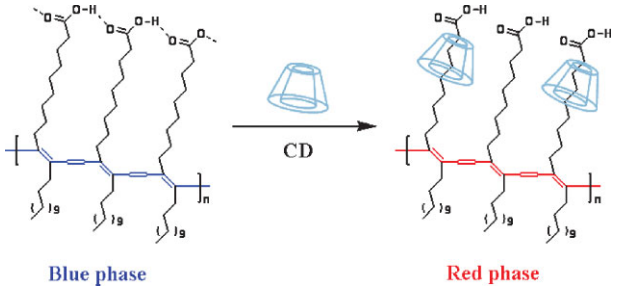
corresponding to a visible absorption maximum at 640 nm. When the temperature is raised from 20 to 95 °C, the absorption maximum of the solution undergoes a gradual blue shift to 540 nm. Upon cooling to 20 °C, the absorption maximum shifts back to 640 nm and the original intensity is recovered. The complete, thermally promoted colorimetric reversibility of this system was demonstrated by repeating the thermal cycles.

The reversible thermochromism of PDA vesicles derived from **20** is very intriguing. The complete recovery of initial absorption at 640 nm after cooling the heat-treated solution (to near boiling temperature of water) indicates that very strong headgroup interactions exist in this PDA. As described above, the internal amide groups in this system should play a significant role in governing colorimetric reversibility. Thus, the strong hydrogen bonds between the amide groups should aid recovery of initial molecular conformation of the PDAs in the cooling phase of the thermal cycle.

A particular interesting feature of the structure of bisdiacetylene **20** and that of the resulting PDAs is the oligoethylene glycol linker. The ethylene glycol linker in the PDAs could serve as a 'holder' for the headgroups and help recovery of the original conformation after thermal cycles. Presumably due to the ethylene glycol linker, the PDA supramolecules display colorimetric reversibility over the wide range in the absorption spectrum (λ_{max}: between 550 and 640 nm).

3.6. A Diagnostic Method for Testing the Colorimetric Reversibility of PDAs

Cyclodextrins (CDs) are intriguing substances because they form inclusion complexes with a variety of substrates.[97,98] In addition,



Scheme 4. A schematic representation of interactions between PCDA **3**-derived PDA and cyclodextrin (CD). Reproduced with permission from [57]. Copyright 2007 American Chemical Society.

the different binding specificities of α-, $\tilde{\beta}$, and γ-cyclodextrins make these substances attractive model systems for studying ligand-receptor interactions. We have recently uncovered unique effects of CDs on the formation and colorimetric response of PDA vesicles derived from PCDA **3**.[99] Interestingly, α-CD was found to completely suppress PCDA polymerization by forming inclusion complexes with self-assembled DA molecules while much higher concentrations of β- and γ-CD show only a negligible effect on the photopolymerization process. Various forms of experimental evidence indicate that α-CD-PCDA complexes are formed. The approximate inner diameters of the α-, β-, and γ-CDs are 0.57, 0.78, and 0.95 nm, respectively. The approximate outer diameters of the CDs are 1.37, 1.53, and 1.69 nm for α-, β-, and γ-CDs, respectively. Owing to the fact that the interchain distances in PCDA supramolecules[100] are ca. 0.5 nm, it is reasonable to expect that α-CD is more capable of perturbing the ordered structures of the DA liposomes than are the β-, and γ-CDs. In the case of β- and γ-CD, it would be more difficult for the CDs to penetrate the densely packed DA layers owing to their larger outer diameters.

More interesting was our observation that α-CD disrupts the ordered structures of polymerized PCDA **3** by forming inclusion complexes (Scheme 4). In addition, α-CD induces the blue-to-red (or purple) color transition of **3**-derived PDAs. Since the chromic transition of PDAs prepared from **3** is irreversible, we were curious to see if α-CD would disturb self-assembled PDA supramolecules that display reversible thermochromism. In experiment probing this question, we made the novel observation that α-CD induces a blue-to-red color transition of PDAs in a selective and predictable manner that depends on the structures of the PDAs.[57] Specifically, we discovered that α-CD induces a blue-to-red color transition of only colorimetrically irreversible PDAs while it has no effect on the colorimetrically reversible PDAs.

In Figure 7 are shown photographs taken after incubation of various PDAs in CD solutions. A blue-to-purple color transition is observed with the solution containing the **3**-derived PDAs and α-CD (Fig. 7A). Surprisingly, the CDs do not promote a color change of a solution of the PDA derived from **7**. In this case, the original color remains unchanged even after a 24 h period (Fig. 7B). This observation demonstrates that CDs are incapable of disturbing the ordered structure of the polymerized lipid assembly arising from **7**.

Interestingly, removal of internal hydrogen-bonding amide groups has an important effect on the ability of CDs to promote the colorimetric change of PDAs. This is seen by observing the

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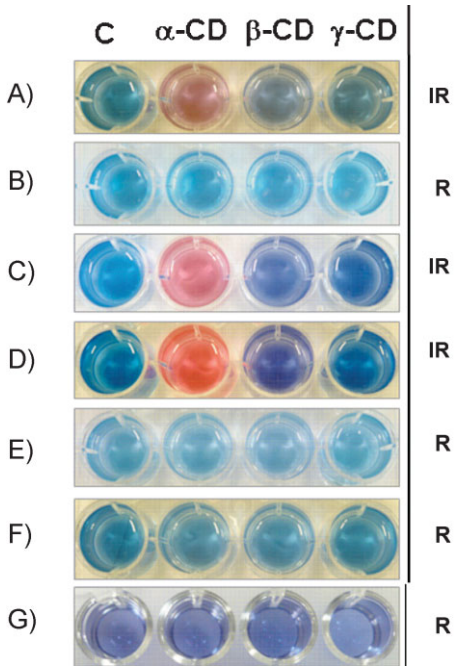

Figure 7. Photographs of suspensions of PDAs (1 mM) derived from various diacetylene monomers in the presence of 10 mM of CDs. Photographs were recorded after 10 min of incubation at 25 °C. Diacetylene monomers used; **3** (A), **7** (B), **8** (C), **9** (D), **16** (E), **11** (F), and **17** (G). R and IR represent reversible and irreversible thermochromism behaviors, respectively, when the monomers are transformed to PDAs and subjected to thermal cycles. Reproduced with permission from [57]. Copyright 2007 American Chemical Society.

color of a solution of the PDA derived from **8**, which changes from blue to purple red in the presence of α-CD (Fig. 7C). The absence of aromatic interactions is also important in governing whether or not α-CD induces a PDA color change. This is demonstrated by the **9**-derived PDA, which undergoes a α-CD promoted blue-to-red color transition (Fig. 7D). Moreover, the color of solutions of PDAs derived from **16** and **11** that display reversible thermochromism are not affected by α-CD (Fig. 7E and F). In addition, a solution of the PDA, derived from naphthyl group containing DA **17**, does not undergo a color transition upon incubation with CDs (Fig. 7G).

In order to gain more information about the effect of CDs on the colorimetric reversibility of PDA supramolecules, a solution containing PDA vesicles derived from **7** and α-CD was subjected to a thermal cycle (25–95–25 °C). If α-CD is capable of disturbing the highly ordered lipid assembly by forming inclusion complexes at high temperature, the PDAs should no longer exhibit reversible thermochromism. In fact, the colorimetric reversibility of **7**-derived PDAs was not affected by α-CD. Thus, it appears that even at high temperatures α-CD does not perturb the ordered structures of those PDAs that have strong headgroup interactions and, as a result, are colorimetrically reversible.

A significant observation made in this effort is that, without exception, the color change of PDAs promoted by α-CD is irreversible. In addition, PDAs capable of strong headgroup interactions do not respond colorimetrically to the CDs. Overall, the results of these studies have not only provided useful information about headgroup interactions in PDA supramolecules, but they have also established an important diagnostic methodology for testing the colorimetric reversibility of PDAs. Specifically, if the addition of α-CD to a solution of the PDA causes a color transition, the PDA is colorimetrically reversible.

4. Colorimetrically Stable PDAs

In aqueous media, the majority of PDA supramolecules reported to date begin to undergo blue-to-red color transitions at or below 70 °C and reach a maximum change (mostly red color) at ca. 90 °C. As described above, strong headgroup interactions in the PDAs are required in order to bring about complete colorimetric reversibility during repeated heating-cooling cycles. The results obtained in studies with **7** suggest that if the carboxyphenylanilido groups are placed at both ends of the DA monomer, much stronger headgroup interactions should exist in the resulting PDA. The bolaamphiphilic DA monomer **21**, expected to adopt a layered structure, was designed to test this proposal (Fig. 8A). In addition, the strong intermolecular interactions between headgroups in the layers of **21** should make the derived polymer supramolecules thermally stable from a colorimetric perspective. Indeed, the colorimetric stability of the PDA supramolecules derived from **21** is dramatic as demonstrated by the observation that no apparent color change takes place even in boiling water.[72]

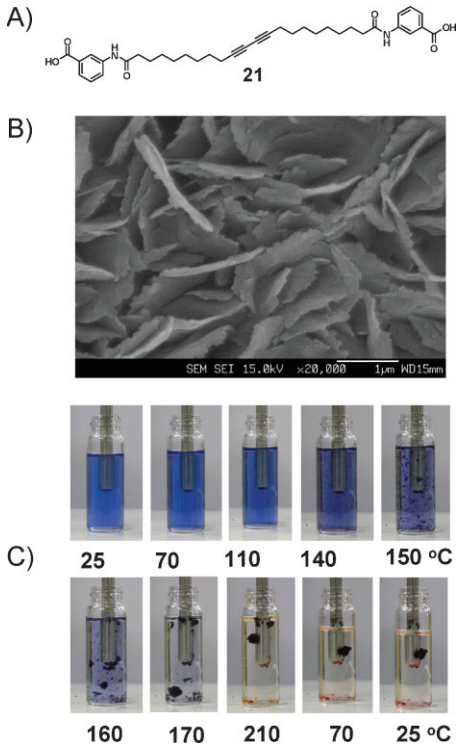

Figure 8. A) Structure of the boloaamphiphilic diacetylene **21**. B) Scanning electron microscope (SEM) image of PDA supramolecules prepared with the bolaamphiphilic diacetylene **21** in ethylene glycol. C) Photographs of PDA suspensions derived from **21** in ethylene glycol upon thermal cycles. Inside the vial is a probe thermometer. Reproduced with permission from [72]. Copyright 2007 Wiley-VCH.

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We have attempted to determine whether the colorimetric stability of this PDA is maintained even at higher temperatures. Ethylene glycol was selected as a solvent for this purpose since it has a much higher boiling point (ca. 200 °C) than water. If PDA supramolecules can be prepared in this solvent, it would be possible to probe the thermal colorimetric stability of the polymer arising from **21** beyond 100 °C. Fortunately, a blue-colored polymer suspension was formed when **21** was subjected to routine procedures for PDA vesicle formation and polymerization. Interestingly, the SEM image of the resulting polymer show that it has a much thinner yet predictable morphology compared to the PDAs prepared in aqueous solutions. Polymers of **21** obtained in ethylene glycol consist of groups of thin rose leaf-like structures with a sub 100 nm thickness (Fig. 8B).

In order to test thermal colorimetric stability, the blue-colored polymer solution derived from **21** in ethylene glycol was heated to 210 °C. As results in Figure 8C show, the blue color of the solution remains unchanged until the solution temperature reaches 140 °C, at which time polymer aggregates start to form, and at 150 °C the solution becomes pale purple. Upon further heating, complete aggregation of the PDA vesicles takes place and the solution becomes clear. Finally, at 210 °C the color of the PDA solution becomes red. Cooling the solution to 25 °C does not lead to recovery of the original blue color and a homogeneous particle distribution. The observations made in our investigations with the PDA derived from the DA monomer **21** should contribute to the knowledge base needed for the rational design of colorimetric sensor materials that operate at high temperatures, thus significantly expanding the colorimetric temperature window of PDA sensor systems.

The colorimetric stability of PDAs derived from structurally related bolaamphiphilic DAs (Fig. 9) was also investigated. In multilayered structures, strong headgroup interactions, caused by hydrogen bonding and π–π aromatic attraction, are expected to play an important role in controlling colorimetric properties of PDAs. In principle, carboxylic acid groups can form head-to-head hydrogen bond networks in multilayered polymer structures. These types of headgroup interactions have been characterized by Shimizu and coworkers using dicarboxylic acid bolaamphiphiles.[101] The importance of hydrogen-bonding between internal amide groups is demonstrated by a comparison of the colorimetric stability of PDA supramolecules, prepared from **21** with that of the polymer derived from the **22**, an ester analogue of **21**. In contrast to the **21**-derived PDAs, PDAs prepared from **22** do not display thermally stimulated colorimetric stability. Accordingly, heating a solution of this PDA from room temperature to 90 °C promotes a blue-to-orange red color change and the original blue color is not completely regenerated when the solution is cooled to 25 °C. The finding that the DCDDA **22**-derived PDA has a lower thermal stability provides evidence for the proposal that hydrogen bonding between internal amide groups are required for high colorimetric stability.

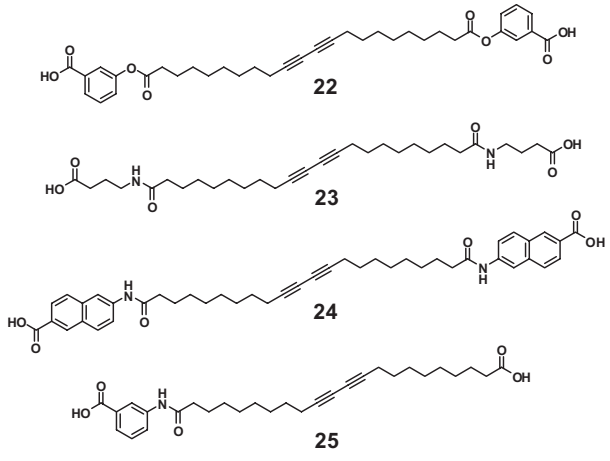

Figure 9. Structures of diacetylene monomers employed to investigate colorimetric stabilities at high temperature.

In addition, the presence of phenyl and naphthyl moieties significantly enhances the colorimetric stability of PDAs. This has been experimentally demonstrated by measuring the colorimetric stability of the PDA prepared from **23**, which does not possess aromatic groups. Thus, when a suspension of polymerized vesicles prepared from **23** is heated to at 90 °C, a blue-to-purple red color change takes place.

The effect of naphthyl groups on colorimetric reversibility was investigated by using a suspension of polymer vesicles generated from **24**. The monomer **24** has two naphthyl groups and, as a result, the degree of aromatic interactions in the resulting PDA is expected to be larger than in the polymer derived from **21**. Also, because the naphthyl group is larger than the phenyl group, steric interactions are disfavored in the PDA arising from **24** versus that coming from the phenyl-substituted DA monomer **21**. Since the **24**-derived PDAs has a thermally induced color stability that is similar to that of the PDA arising from **21**, it appears that sterically disfavored interactions in the naphthyl analog are compensated for by the stabilizing effect associated with extended π–π aromatic interactions.

The results obtained from investigations with PDAs, formed from the mono-substituted 10,12-docosadiyndioic acid (DCDDA) monomer **25**, are intriguing. PDAs obtained from **25** display complete colorimetric reversibility. Although a high colorimetric stability is not observed with this substance, the reversibility of the color transition with the PDAs derived from **25** suggests that when strong headgroup interactions exist at one end of a bolaamphiphilic DCDDA, colorimetric reversibility takes place. Since unsubstituted carboxylic acids are subject to further functionalization, the results obtained in studies with the PDAs that come from the unsymmetric bolaamphiphilic DA monomer **25** provide a foundation for the design of colorimetrically reversible bolaamphiphilic PDA supramolecules.

5. Colorimetrically Sensitive PDAs

In general, preparation of colorimetrically sensitive PDAs is a much easier task than the construction of colorimetrically reversible or stable PDA polymers. The design of PDAs that display thermally sensitive colorimetric responses can be achieved by using three general guiding principles. First, the PDAs derived from DA monomers having diacetylene functional groups near the headgroup tend to show reduced colorimetric stability in comparison to PDAs prepared from DA monomers in which diacetylene moieties are located in the middle or near the middle of

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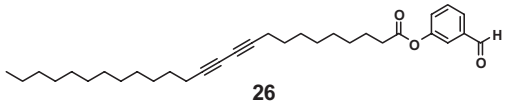
alkyl chains. Comparison of the colorimetric stabilities of PDAs obtained from **17** and **19** is a representative example of this family. Specifically, the PDA derived from **19** is more sensitive to thermally stimulated color change than that arising from the **17**-derived PDA.[70] Thus, the PDA solution obtained from **19** displays a purple-red color at 70 °C. In contrast, the **17**-derived PDA solution requires 90 °C to show the similar purple-red color.

Second, the colorimetric sensitivity of the PDA supramolecules can be manipulated by varying headgroup interactions. For example, the PDA derived from DA monomer **26** lacks strong headgroup interactions in the molecularly assembled state. This is a consequence of the fact that no hydrogen bondable amids or carboxylic acids are present. As expected the PDAs derived from **26** undergo blue-to-red color transitions at ca. 45 °C, a temperature that is much lower than the chromic transition temperatures of most PDA molecules.[73] Third, colorimetric transition temperatures of PDAs can be controlled by adjusting conditions used for PDA synthesis. In general, PDAs prepared at high temperatures have enhanced colorimetric stabilities compared to those obtained by polymerization at low temperatures.



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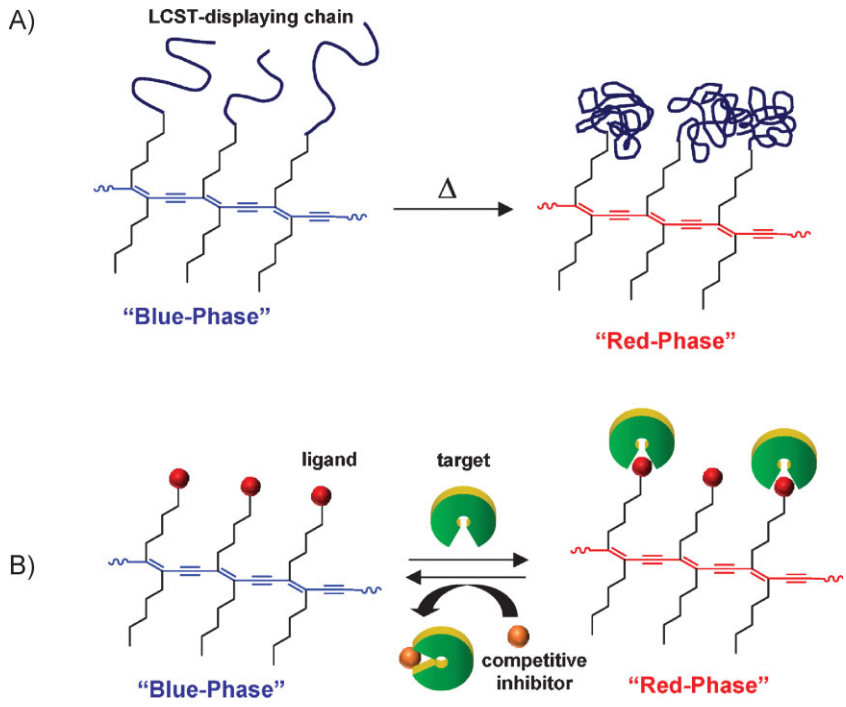
6. Conclusions and Future Challenges

In this Feature Article, we have described strategies that have been developed for controlling color transitions of PDA supramolecules. The major focus has been on strategies based on headgroup hydrogen bonding and aromatic $\pi-\pi$ interactions that have been discovered in studies carried out by our group. In our efforts in this area, we have been able to manipulate both the colorimetric reversibility and the color transition temperatures of PDAs, simply by modifying the degree of headgroup interactions. The conclusions drawn from our work suggest that strong headgroup interactions are essential for reversible thermochromism and enhanced colorimetric stability of the PDA supramolecules in aqueous media. A simple and straightforward method, based on cyclodextrin-PDA interactions, has been devised for the differentiation of colorimetric reversibility of PDAs.

A remaining challenge in the area of PDA thermochromism is the design of PDAs that display sharp blue-to-red color transitions at specific temperatures. Without exception, the PDAs described thus far undergo gradual blue-to-red color changes, through an intermediate purple color, upon thermal stimulation. A PDA sensor that displays an abrupt color (phase) change at a designated temperature would be a potentially useful temperature sensor. Moreover, since PDAs in their red-phase are fluorescent, phase changes can be easily detected using fluorescence microscopy. This property could potentially enable the monitoring of the temperature inside a microchannel, without the need for using a thermocouple. Immobilization of PDAs that possess functional groups, which are associated with a lower critical solution temperature (LCST),[102] on the vesicles might be a possible solution to this problem. Abrupt aggregation of LCST groups on the surfaces occurring at a specific temperature might induce a subsequent sharp color transition of the PDA supramolecules (Scheme 5A).

Applications of colorimetrically reversible PDAs to monitoring changes in biologically important target molecules, such as proteins, nucleic acids, carbohydrates and cells, remains as an another significant scientific challenge in this area. The development of PDA systems that display reversible color transitions upon ligand-receptor interactions, without any doubt, would find great utility in novel binding assay systems (Scheme 5B). However, the design of PDA systems that maintain colorimetric reversibility throughout the range of binding and unbinding processes is a challenging endeavor. Fortunately, PDA sensors can be constructed using a combination of matrix DA monomers and ligand/receptor containing lipid molecules. By adjusting the ratios of the types of monomers that lead to colorimetric reversibility and functional lipid molecules, it should be possible to develop colorimetrically reversible affinochromic PDA sensor systems.



Scheme 5. Schematic representations of PDAs designed for sharp colorimetric transition (A) and for monitoring of reversible ligand-receptor interactions (B).

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[1] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491.
[2] S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324.
[3] F. Hide, M. A. Díaz-García, B. J. Schwartz, A. J. Heeger, *Acc. Chem. Res.* **1997**, *30*, 430.
[4] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed.* **1998**, *37*, 402.
[5] P. F. Barbara, A. J. Gesquiere, S.-J. Park, Y. J. Lee, *Acc. Chem. Res.* **2005**, *38*, 602.
[6] S. W. Thomas III, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, *107*, 1339.
[7] H.-A. Ho, A. Najari, M. Leclerc, *Acc. Chem. Res.* **2008**, *41*, 168.
[8] L. M. Goldenberg, M. R. Bryce, M. C. Petty, *J. Mater. Chem.* **1999**, *9*, 1957.
[9] B. Liu, G. C. Bazan, *Chem. Mater.* **2004**, *16*, 4467.
[10] A. Herland, O. Inganäs, *Macromol. Rapid Commun.* **2007**, *28*, 1703.
[11] A. Rose, Z. Zhu, C. F. Madigan, T. M. Swager, V. Bulović, *Nature* **2005**, *434*, 876.
[12] C. Fan, K. W. Plaxco, A. J. Heeger, *J. Am. Chem. Soc.* **2002**, *124*, 5642.
[13] B. Liu, G. C. Bazan, *J. Am. Chem. Soc.* **2006**, *128*, 1188.
[14] I.-B. Kim, U. H. F. Bunz, *J. Am. Chem. Soc.* **2006**, *128*, 2818.
[15] C. Tan, E. Atas, J. G. Müller, M. R. Pinto, V. D. Kleiman, K. S. Schanze, *J. Am. Chem. Soc.* **2004**, *126*, 13685.
[16] J. K. Lee, T. S. Lee, *J. Polym. Sci. Part A* **2005**, *43*, 1397.
[17] C.-C. Pun, K. Lee, H.-J. Kim, J. Kim, *Macromolecules* **2006**, *39*, 7461.
[18] D. J. Ahn, J.-M. Kim, *Acc. Chem. Res.* **2008**, *41*, 805.
[19] R. W. Carpick, D. Y. Sasaki, M. S. Marcus, M. A. Eriksson, A. R. Burns, *J. Phys. Condens. Matter* **2004**, *16*, R679.
[20] A. Mueller, D. F. O'Brien, *Chem. Rev.* **2002**, *102*, 727.
[21] R. Jelinek, S. Kolusheva, *Biotechnol. Adv.* **2001**, *19*, 109.
[22] H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 113.
[23] S. Okada, S. Peng, W. Spevak, D. Charych, *Acc. Chem. Res.* **1998**, *31*, 229.
[24] W. Zhou, Y. Li, D. Zhu, *Chem. Asian J.* **2007**, *2*, 222.
[25] G. Wegner, *Makromol. Chem.* **1972**, *154*, 35.
[26] D. Day, H. Ringsdorf, *J. Polym. Sci. Polym. Lett. Ed.* **1978**, *16*, 205.
[27] A. Sun, J. W. Lauher, N. S. Goroff, *Science* **2006**, *312*, 1030.
[28] Y. Lu, Y. Yang, A. Sellinger, M. Lu, J. Huang, H. Fan, R. Haddad, G. Lopez, A. R. Burns, D. Y. Sasaki, J. Shelnutt, C. J. Brinker, *Nature* **2001**, *410*, 913.
[29] Y. Okawa, M. Aono, *Nature* **2001**, *409*, 683.
[30] T. Kim, K. C. Chan, R. M. Crooks, *J. Am. Chem. Soc.* **1997**, *119*, 189.
[31] O. Endo, H. Ootsubo, N. Toda, M. Suhara, H. Ozaki, Y. Mazaki, *J. Am. Chem. Soc.* **2004**, *126*, 9894.
[32] K. Morigaki, T. Baumgart, A. Offenhäusser, W. Knoll, *Angew. Chem. Int. Ed.* **2001**, *40*, 172.
[33] S. H. Kang, B. M. Jung, J. Y. Chang, *Adv. Mater.* **2007**, *19*, 2780.
[34] A. Sarkar, S. Okada, H. Nakanishi, H. Matsuda, *Macromolecules* **1998**, *31*, 9174.
[35] J. M. Schnur, B. R. Ratna, J. V. Selinger, A. Singh, G. Jyothi, K. R. K. Easwaran, *Science* **1994**, *264*, 945.
[36] G. Ma, A. M. Műller, C. J. Bardeen, Q. Cheng, *Adv. Mater.* **2006**, *18*, 55.
[37] J. Song, J. S. Cisar, C. R. Bertozzi, *J. Am. Chem. Soc.* **2004**, *126*, 8459.
[38] M. Arai, S. Okada, *Chem. Lett.* **2006**, 1012.
[39] H. Gan, H. Liu, Y. Li, Q. Zhao, Y. Li, S. Wang, T. Jiu, N. Wang, X. He, D. Yu, D. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 12452.
[40] B. N. Thomas, R. C. Corcoran, C. L. Cotant, C. M. Lindemann, J. E. Kirsch, P. J. Persichini, *J. Am. Chem. Soc.* **1998**, *120*, 12178.
[41] P. Yager, P. E. Schoen, *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 371.
[42] D. A. Frankel, D. F. O'Brien, *J. Am. Chem. Soc.* **1994**, *116*, 10057.
[43] M. Masuda, T. Hanada, K. Yase, T. Shimizu, *Macromolecules* **1998**, *31*, 9403.
[44] M. Shirakawa, N. Fujita, S. Shinkai, *J. Am. Chem. Soc.* **2005**, *127*, 4164.
[45] S. B. Lee, R. Koepsel, D. B. Stolz, H. E. Warriner, A. J. Russell, *J. Am. Chem. Soc.* **2004**, *126*, 13400.
[46] R. R. Chance, R. H. Baughman, H. Müller, C. J. Eckhardt, *J. Chem. Phys.* **1977**, *67*, 3616.
[47] D.-C. Lee, S. K. Sahoo, A. L. Cholli, D. J. Sandman, *Macromolecules* **2002**, *35*, 4347.
[48] R. R. Chance, *Macromolecules* **1980**, *13*, 396.
[49] J. Yoon, S. K. Chae, J.-M. Kim, *J. Am. Chem. Soc.* **2007**, *129*, 3038.
[50] A. D. Nava, M. Thakur, A. E. Tonelli, *Macromolecules* **1990**, *23*, 3055.
[51] C. A. Sandstedt, C. J. Eckhardt, M. J. Downey, D. J. Sandman, *Chem. Mater.* **1994**, *6*, 1346.
[52] D. Bloor, *Macromol. Chem. Phys.* **2001**, *202*, 1410.
[53] Y. Tomioka, N. Tanaka, S. Imazeki, *Thin Solid Films* **1989**, *179*, 27.
[54] H. Müller, C. J. Eckhardt, *Mol. Cryst. Liq. Cryst.* **1978**, *45*, 313.
[55] R. A. Nallicheri, M. F. Rubner, *Macromolecules* **1991**, *24*, 517.
[56] R. W. Carpick, D. Y. Sasaki, A. R. Burns, *Langmuir* **2000**, *16*, 1270.
[57] S. Lee, J.-M. Kim, *Macromolecules* **2007**, *40*, 9201.
[58] D. H. Charych, J. O. Nagy, W. Spevak, M. D. Bednarski, *Science* **1993**, *261*, 585.
[59] A. Reichert, J. O. Nagy, W. Spevak, D. Charych, *J. Am. Chem. Soc.* **1995**, *117*, 829.
[60] J. J. Pan, D. Charych, *Langmuir* **1997**, *13*, 1365.
[61] Z. Ma, J. Li, M. Liu, J. Cao, Z. Zou, J. Tu, L. Jiang, *J. Am. Chem. Soc.* **1998**, *120*, 12678.
[62] C. Wang, Z. Ma, *Anal. Bioaanl. Chem.* **2005**, *382*, 1708.
[63] Y. K. Jung, T. W. Kim, J. Kim, J.-M. Kim, H. K. Park, *Adv. Funct. Mater.* **2008**, *18*, 701.
[64] Q. Cheng, R. C. Stevens, *Adv. Mater.* **1997**, *9*, 481.
[65] S. Kolusheva, T. Shahal, R. Jelinek, *J. Am. Chem. Soc.* **2000**, *122*, 776.
[66] S. Y. Okada, R. Jelinek, D. Charych, *Angew. Chem. Int. Ed.* **1999**, *38*, 655.
[67] I. Gill, A. Ballesteros, *Angew. Chem. Int. Ed.* **2003**, *42*, 3264.
[68] S. Kolusheva, R. Kafri, M. Katz, R. Jelinek, *J. Am. Chem. Soc.* **2001**, *123*, 417.
[69] S. W. Lee, C. D. Kang, D. H. Yang, J.-S. Lee, J. M. Kim, D. J. Ahn, S. J. Sim, *Adv. Funct. Mater.* **2007**, *17*, 2038.
[70] J.-M. Kim, J.-S. Lee, H. Choi, D. Sohn, D. J. Ahn, *Macromolecules* **2005**, *38*, 9366.
[71] D. J. Ahn, E.-H. Chae, G. S. Lee, H.-Y. Shim, T.-E. Chang, K.-D. Ahn, J.-M. Kim, *J. Am. Chem. Soc.* **2003**, *125*, 8976.
[72] H. Park, J.-S. Lee, H. Choi, D. J. Ahn, J.-M. Kim, *Adv. Funct. Mater.* **2007**, *17*, 3447.
[73] H. O. Yoo, S. K. Chae, J.-M. Kim, D. J. Ahn, *Macromol. Res.* **2007**, *15*, 478.
[74] M. F. Rubner, *Macromolecules* **1986**, *19*, 2129.
[75] G. J. Exarhos, W. M. Risen, Jr, R. H. Baughman, *J. Am. Chem. Soc.* **1976**, *98*, 481.
[76] Q. Huo, K. C. Russel, R. M. Leblanc, *Langmuir* **1999**, *15*, 3972.
[77] H. W. Beckham, M. F. Rubner, *Macromolecules* **1993**, *26*, 5198.
[78] B. J. Orchard, S. K. Tripathy, *Macromolecules* **1986**, *19*, 1844.
[79] S. H. W. Hankin, M. J. Downey, D. J. Sandman, *Polymer* **1992**, *33*, 5098.
[80] M. K. Beyer, H. Clausen-Schaumann, *Chem. Rev.* **2005**, *105*, 2921.
[81] R. H. Baughman, R. R. Chance, *J. Polym. Sci. Polym. Phys. Ed.* **1976**, *14*, 2037.
[82] J. Olmsted III, M. Strand, *J. Phys. Chem.* **1983**, *87*, 4790.

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[83] J.-M. Kim, Y. B. Lee, D. H. Yang, J.-S. Lee, G. S. Lee, D. J. Ahn, *J. Am. Chem. Soc.* **2005**, *127*, 17580.
[84] A. Saito, Y. Urai, K. Itoh, *Langmuir* **1996**, *12*, 3938.
[85] A. Lio, A. Reichert, D. J. Ahn, J. O. Nagy, M. Salmeron, D. H. Charych, *Langmuir* **1997**, *13*, 6524.
[86] H. Tanaka, M. A. Gomez, A. E. Tonelli, M. Thakur, *Macromolecules* **1989**, *22*, 1208.
[87] Z. Yuan, C.-W. Lee, S.-H. Lee, *Angew. Chem. Int. Ed.* **2004**, *43*, 4197.
[88] Y. Gu, W. Cao, L. Zhu, D. Chen, M. Jiang, *Macromolecules* **2008**, *41*, 2299.
[89] J. K. Lim, Y. Lee, K. Lee, M. Gong, S.-W. Joo, *Chem. Lett.* **2007**, 1226.
[90] H. Peng, J. Tang, J. Pang, D. Chen, L. Yang, H. S. Ashbaugh, C. J. Brinker, Z. Yang, Y. Lu, *J. Am. Chem. Soc.* **2005**, *127*, 12782.
[91] H. Peng, J. Tang, L. Yang, J. Pang, H. S. Ashbaugh, C. J. Brinker, Z. Yang, Y. Lu, *J. Am. Chem. Soc.* **2006**, *128*, 5304.
[92] U. Jonas, K. Shah, S. Norvez, D. H. Charych, *J. Am. Chem. Soc.* **1999**, *121*, 4580.
[93] A. Singh, R. B. Thompson, J. M. Schnur, *J. Am. Chem. Soc.* **1986**, *108*, 2785.
[94] One representative example of visible absorption spectra displaying an isosbestic point from colorimetrically irreversible PDAs can be found in our previous report. J.-M. Kim, Y. B. Lee, S. K. Chae, D. J. Ahn, *Adv. Funct. Mater.* **2006**, *16*, 2103. See Figure 3A in the cited reference.
[95] Several examples of gradual blue shift of absorption maxima from colorimetrically reversible PDAs are described in Figure 5 in ref. [70]. In addition, the results described in ref. [96] also support this observation.
[96] C. H. Lee, J. S. Kim, S. Y. Park, D. J. Ahn, J.-M. Kim, *Chem. Lett.* **2007**, 682.
[97] Special issue on cyclodextrins, *Chem. Rev.* **1998**, *98*, issue 5, pp.1743–2076.
[98] A. Harada, *Acc. Chem. Res.* **2001**, *34*, 456.
[99] J.-M. Kim, J.-S. Lee, J.-S. Lee, S.-Y. Woo, D. J. Ahn, *Macromol. Chem. Phys.* **2005**, *206*, 2299.
[100] A. Berman, D. J. Ahn, A. Lio, M. Salmeron, A. Reichert, D. Charych, *Science* **1995**, *269*, 515.
[101] M. Kogiso, S. Ohnishi, K. Yase, M. Masuda, T. Shimizu, *Langmuir* **1998**, *14*, 4978.
[102] E. S. Gil, S. M. Hudson, *Prog. Polym. Sci.* **2004**, *29*, 1173.

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