CHAPTER II

LITERATURE REVIEW

Color transition of PDA assemblies

Thermochromism is one of the most extensively explored properties of PDA vesicle prepared from PCDA monomers. [5,9] The increasing temperature of the poly(PCDA) vesicle solution causes significant blue shift of absorption spectra at 60 ^{o}C where it appears purple to naked eyes. It turns to red color at temperature above 80 ^{o}C. This color transition is normally an irreversible process. The maximum absorption of blue and red forms of poly(PCDA) vesicles in water is generally observed near 635 and 540 nm, respectively, as shown in Fig. 5.

Mechanism of the color transition of poly(PCDA) vesicles has been proposed as illustrated in Fig. 6. The interactions between head groups of poly(PCDA) are relatively weak. Thus, the release of mechanical strain upon thermal stimulation results in C-C bond rotation of the polymer backbone and weakening of head group 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 ^{o}C). The release of the mechanical strain in the side chain causes significant twisting of the conjugated π-orbital arrays, which results in drastic decrease of conjugation length. The poly(PCDA) vesicles appear red at this state.

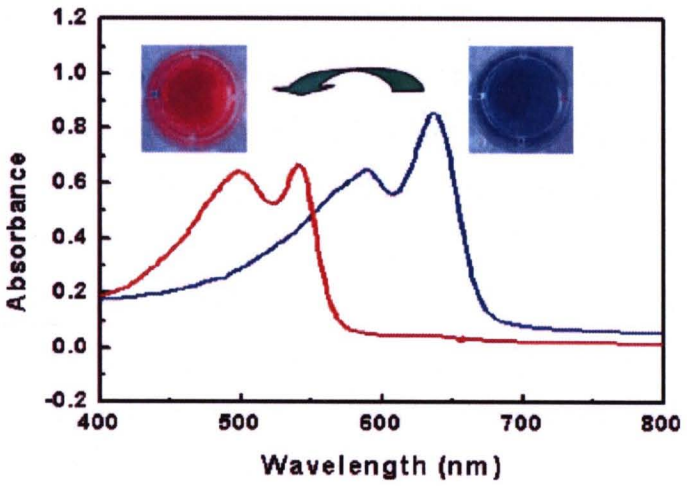

Figure 5 Absorption spectra of poly(PCDA) vesicles in (left) red and (right) blue forms [5]

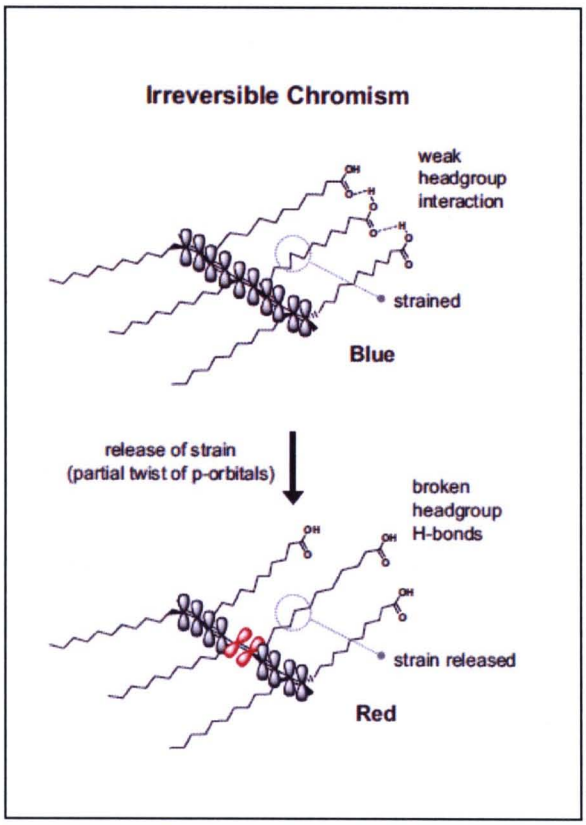

Figure 6 Schematic representations of the mechanisms of chromic responses of irreversible PDA [5]

Controlling color transition by structural modification

The control of color-transition behaviors of PDA assemblies can be achieved via structural modification. Recent work by Ahn et al. [11] demonstrated that the modification of PCDA head group by attaching anilide and carboxylanilides (ortho-, meta- and para-) (see Fig.7) greatly affected the color transition. The assemblies prepared from PCDA, PCDA-aniline, PCDA-oBzA, PCDA-pBzA exhibited irreversible color transition upon increasing temperature. The transition temperature also varied with type of the head groups, depending on strength of the interaction at surface. In the case of PCDA-mBzA, it was found that the color transition occurred in a reversible fashion. They reasoned that the hydrogen-bonding of the carboxylic head groups within the assemblies was very strong, allowing the molecular organizations to relax back to original state upon cooling to room temperature. The authors recommended that the orientation of the terminal carboxyl and amide groups in meta-carboxylanilide was suitable for a formation of double hydrogen-bonding required for the recovery of the original conformation as shown in Fig. 7.

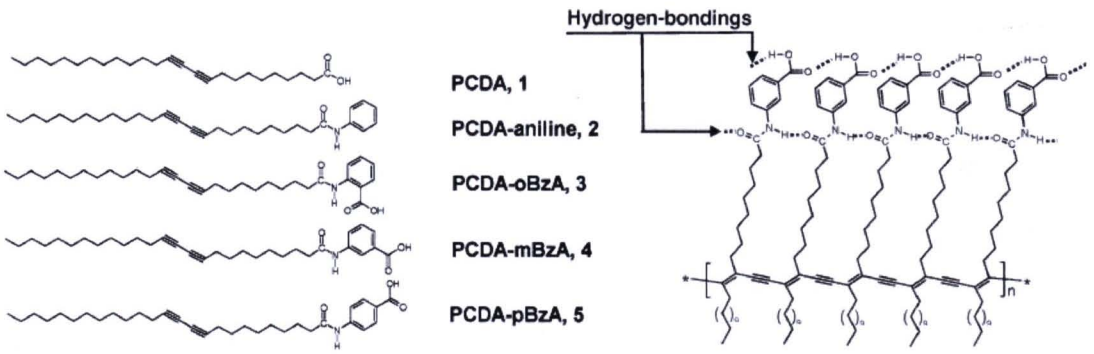

Figure 7 Structure of diacetylene monomer and schematic of enhanced hydrogen-bonding at terminal carboxyl and amide-carbonyl groups [11]

In their continuation studies, they further evaluated in great detail on the effect of structural modification on thermochromism of PDA assemblies. Various types of monomers (see Fig. 8) were synthesized in order to investigate the effects of 1) amide hydrogen bonding, 2) aromatic interactions, 3) alkyl chain lengths, and 4) carboxylic groups and naphthyl group. [12] The thermochromic properties of the PDA assemblies investigated by using UV/vis absorption spectroscopy suggested that cooperative

interactions between amide, aromatic and carboxlic acid head groups were the requirement for reversibility of PDA. They found that different PDA assemblies showed partial reversible thermochromism, irreversible thermochromism and reversible thermochromism, depending on their structure. The removal of amide group resulted in a partial reversible thermochromism while the removal of aromatic group caused irreversible thermochromism. The variation of alkyl chain length hardly affected the reversibility of the PDA assemblies. The modification of head groups by attaching naphthyl groups enhanced aromatic interaction, leading to the reversible thermochromism.

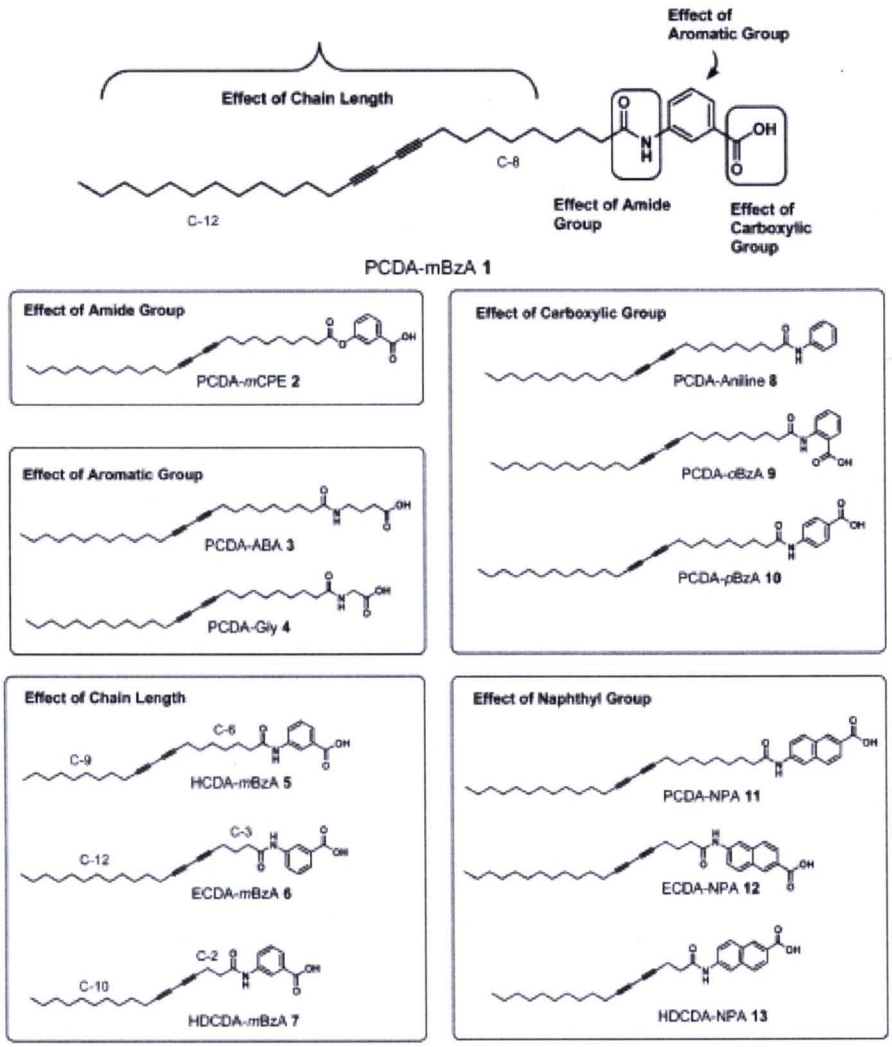

Figure 8 Structures of PDA monomers with different head groups and alkyl chain [12]

The structures of DA monomers were also modified by attaching two head groups as shown in Fig. 9. [13] This class of DA monomers yielded PDA assemblies with different morphologies such as spherically-shaped, a leaf-like morphology and fibrous morphology. The existence of two head groups promoted the interfacial interaction within the assemblies, which significantly affected their color transition. The PDA assemblies prepared from DCDDA-bis-mCPE 4 and DCDDA-bis-ABU 5 still exhibited irreversible color transition upon increasing temperature. In the case of PCDA-mBzA 1, DCDDA-bis-mBzA 3, DCDDA-bis-NPA 6 and DCDDA-mono-mBzA 7, their PDA assemblies showed the reversible color transition. In addition, the DCDDA-bismBzA 3 and DCDDA-bis-NPA 6 showed reversible color transition at much higher temperature compared to that of similar monomers with single head group. The high thermal stability is attributed to strong head group interactions (hydrogen bonding and aromatic interaction) that are introduced during the self assembling process.

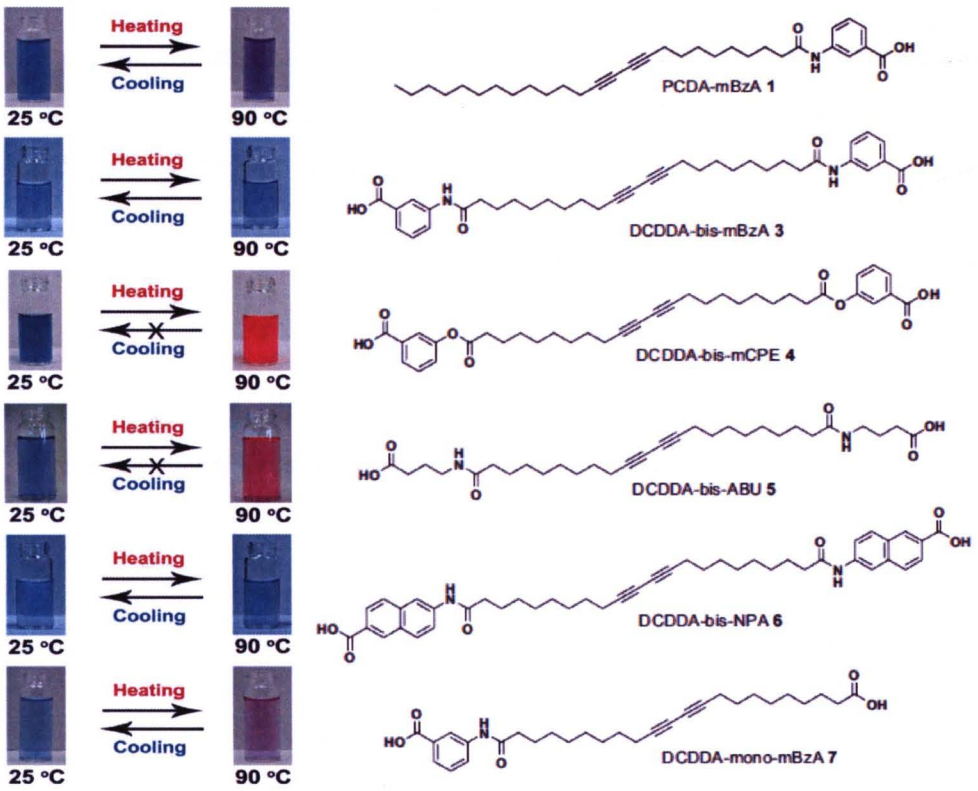

Figure 9 Structures of DA monomers with one and two head group [13]

The control of color-transition behaviors of PDA assemblies can be achieved by attaching head group together. Singh and coworker [14] modified DA monomer by using this approach as shown in Fig. 10. PDA assemblies obtained from bisdiacetylenic phossphorylcholine were prepared in aqueous solution. The color transition from blue to red, which is a reversible process, takes place at about 50 °C.

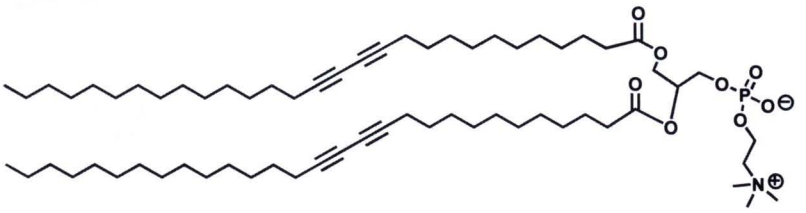

Figure 10 Structure of bisdiacetylenic phossphorylcholine [14]

Z. Yuan et al. [15] demonstrated the modification of PCDA by attaching terephthalic acid substituted in side chains (see Fig. 11). The PDA assemblies exhibited rigid backbone and showed reversible color transition upon increasing temperature. They found that the double H-bonds between the acid hard cores DA recognition allowed for retaining more favorable packing of the reactive groups in spin-coated films or even in dispersed solutions with a high degree of local ordering.

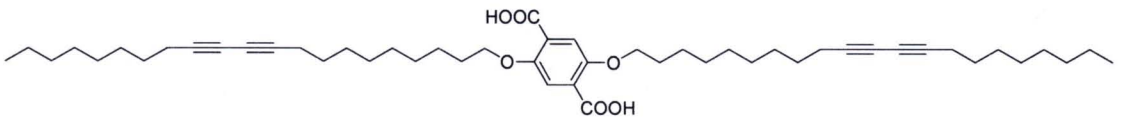

Figure 11 Structure of diacetylene D(9,8)diacids monomer [15]

Moreover, Z. Yuan et al. observed the ability to construct very stable dispersions of supramolecular polymers from the doubly hydrogen bonded complex of terephthalic acids containing DA groups. [16] The assemblies exhibited reversible color transition. The reversible change between blue and red forms under acid–base treatments can be explained by the change in the structure of the core group affecting the packing of the side PDA chain. Fig. 12 illustrates the structure of PDA in the presence of HCl and NH_3. The NH_3 vapor eliminates HCl molecules from the complex structure and the increase in motional freedom of the side PDA chains allows a more disordered and less coplanar polymer with a lower conjugation length thereby producing a red form.

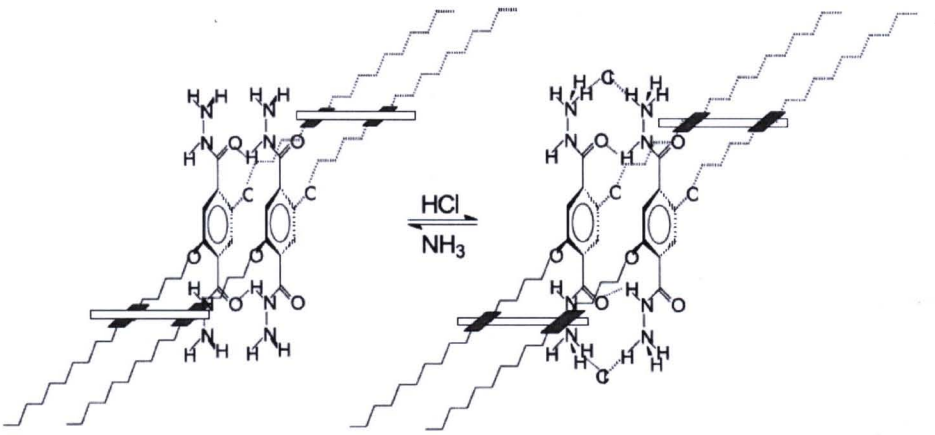

Figure 12 Structure of PDA hydrazide dimer in the presence of HCl and NH_3 [16]

Preparation of PDA assemblies in thin films

In addition to the preparation of PDA assemblies in aqueous solution, it can be prepared in thin film. Many research groups have demonstrated the preparation of PDA assemblies in thin films by adding different matrices. J.-M. Kim and coworker studied PDA-embedded polymer films which can be obtained by simply mixing PDA with polyvinyl alcohol (PVA). [17] The embedment of PDA supramolecules in PVA films was carried out by a mixing–drying process. A typical method and photographs of a resultant PDA solution and a PDA-embedded PVA film are shown in Fig. 13. The blue-colored thin polymer films formed in this manner undergo the typical PDA blue-to-red transition upon thermal stress. As compared to a solution of PDA assemblies, the film requires a higher temperature of about 10 °C to promote a complete color transition to red.

Moreover, Y. Gu and coworkers studied thermochromism in a self-assembled poly(vinylpyrolidone)(PVP) and PDA.[18] They found that the thin film showed reversible thermochromism and stabilized at high temperatures (up to 120 °C). The physical constraint exerted on every PDA bilayers by the PVP mortar substantially assisted reversible conformational transitions in the PDA main chain. Fig. 14 shows the "bricks and mortar" morphology (PDA bilayers as the bricks and PVP as the mortar). In this "bricks and mortar" structure, the carboxylic acid head groups in the side chains of each PDA bilayer were hydrogen-bonded to PVP chains.

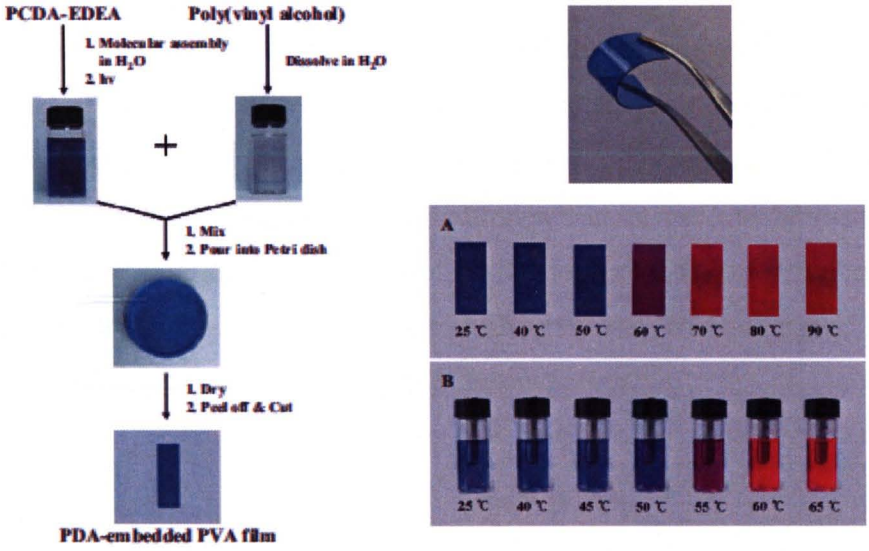

Figure 13 Fabrication of PDA-embedded PVA films (a) Photographs of the PDA embedded polyvinyl alcohol film (b) the PDA assemblies solution during heating process [17]

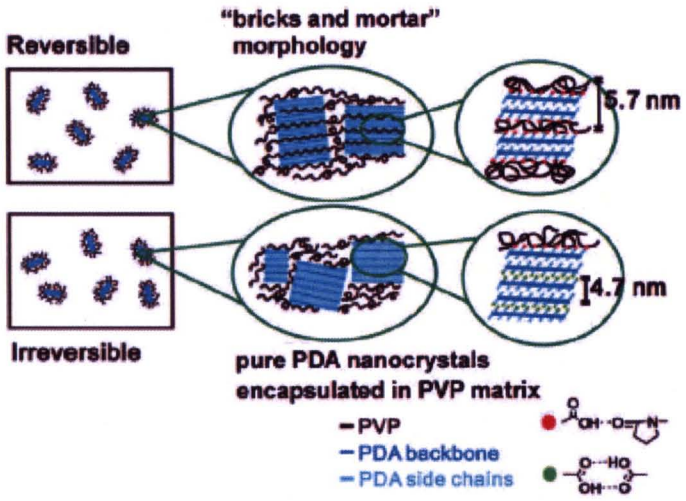

Figure 14 Schematic illustration of the "Bricks and Mortar" morphology showing the reversible and irreversible thermochromism [18]

S. Wu and coworkers prepared hydrogen-bonding complexes of the DA and poly(4-vinylpyridine) (P4VP) in organic solvents.[19] The complexes were spin-cast and formed high-quality thin films. The film showed irreversible color transition upon increasing temperature. Fig. 15 illustrates a model of the P4VP-TDA hydrogen-

bonding complex. They suggest that TDA self-assembles and forms microcrystalline domains in the hydrogen-bonding complex. The blue phase PDA in P4VP-TDA changes to the red phase of PDA after heating to 100 °C. The color does not change back to blue after cooling to room temperature. Therefore, this irreversible thermochromism in the hydrogen-bonding complex can be used to fabricate patterns with different PDA phases. When the thin films were exposed to different solvents such as ethyl acetate, ethanol and THF, some films showed color changes. Therefore, they can be utilized as sensor for detecting different solvents.

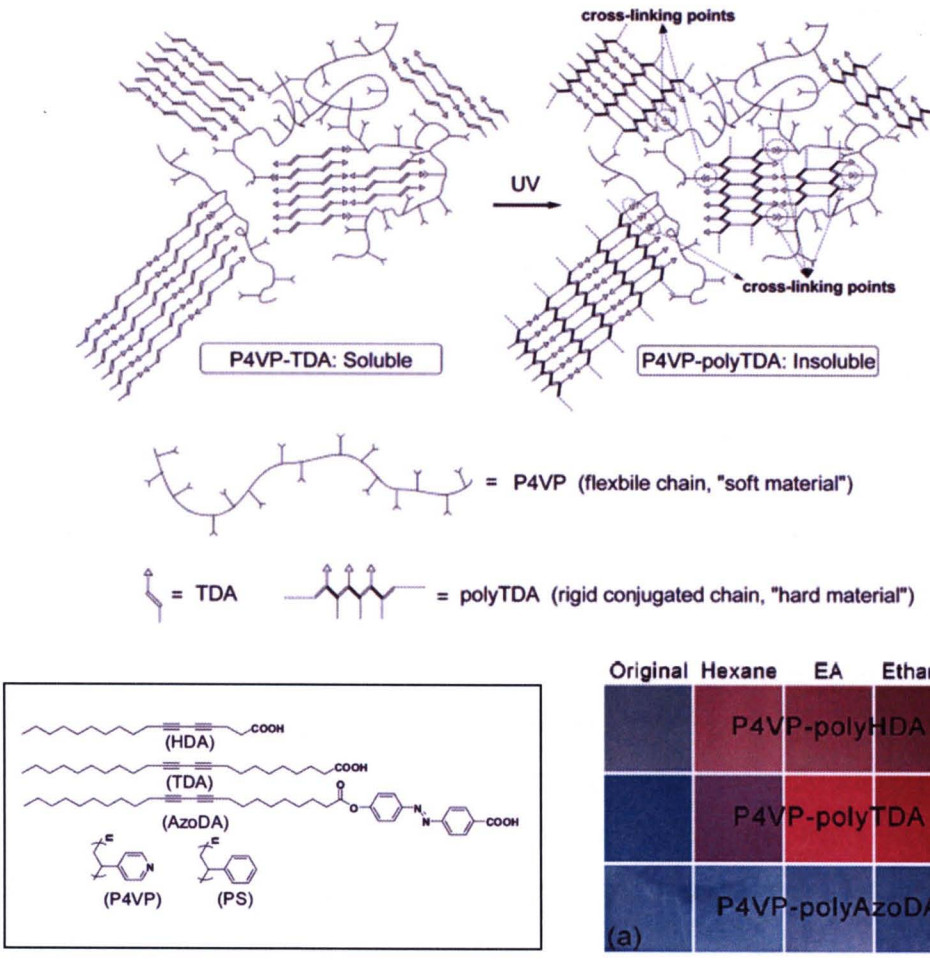

Figure 15 Model of the hydrogen-bonding complex P4VP-TDA and photographs of hydrogen-bonding complexes before and after exposure to different organic solvents [19]

Fluorescence properties of PDA assemblies

Fluorescence spectroscopy is another technique used to analyze colorimetric response properties of PDA assemblies. It has observed that the PDA assemblies become fluorescent in the red form in addition to the color change. However, the fluorescent intensity is rather weak. Therefore, many researchers attempt to increase fluorescent signal by adding foreign fluorophores in PDA assemblies. X. Li and coworkers study fluorescence resonance energy transfer (FRET) in PDA liposomes synthesized using different molar ratios of dansyl-tagged diacetylene and diacetylene-carboxylic acid monomers [20]. Fig. 16 illustrates the representation of a PDA liposome prepared with a mixture of the fluorescent DA and PDA. The "*Off*" state represents when FRET efficiency (*E*) from dansyl to PDA is low, and the "*On*" state represents when *E* is large. They attributed this to the insertion of dansyl in the bilayer of the liposomes, which led to an increased dansyl quantum yield and a higher interaction of multiple acceptors with limited available donors. They found that the FRET amplification of PDA emissions after heating the solution was much higher when dansyl was linked to DA through longer and flexible linkers than through shorter linkers.

In addition, G. Ma and Q. Cheng [21] demonstrated a nanoscale lipid membrane-based sensor of PDA vesicles for fluorescence detection of organic amines. The vesicle sensor was constructed by incorporation of a BODIPY fluorescent dye into the PDA vesicles. The assemblies exhibited drastic increase of fluorescent intensity upon increasing solution pH (see Fig. 17). The fluorescent properties of the vesicles can be manipulated by adjusting lipid components and controlling environments. The fluorescence recovery process was reversible and highly sensitive. The vesicle sensor was applied for detecting an organic amine, triethylamine (TEA). A linear relationship between the increase in fluorescence intensity and the concentrations of TEA was obtained.

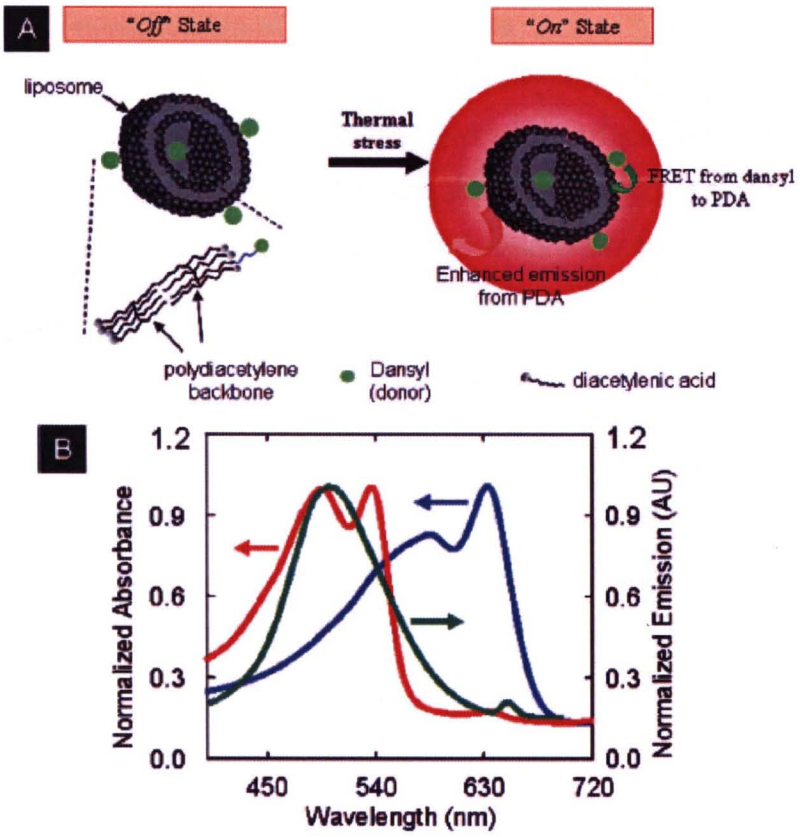

Figure 16 (A) Schematic representation of a PDA liposome prepared with a mixture of the fluorescent DA and PDA (B) Normalized absorption spectra of blue (blue curve) and red forms (red curve) PDA and emission spectrum of dansyl fluorophores (green curve) attached to PDA liposomes (λ_{ex} = 337nm) [20]

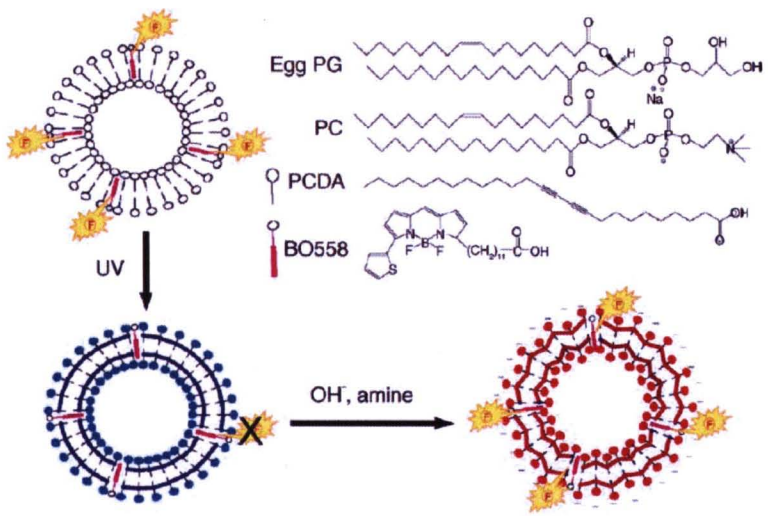

Figure 17 Schematic illustration of the vesicle sensor [21]

Recent structural modification of PDA assemblies

Recently, S. Wascharasindhu and coworkers synthesized mono- and diamides derivatives of PCDA from condensation of PCDA with various aliphatic and aromatic diamines (see Fig. 18). [22] They studied the thermochromic properties of the PDA assemblies in aqueous solution by using UV/vis absorption spectroscopy. The color transition temperatures and thermochromic reversibility of the PDA assemblies varied with number of amide groups and the structure of the aliphatic and aromatic linkers. The phenylenediamide and polymethylenediamide PCDA derivatives gave PDA assemblies with complete thermochromic reversibility while the PDA assemblies obtained from 1, 2-cyclohexylene and glycolic chain diamide derivatives exhibited irreversible thermochromism. The PDA assemblies obtained from the aromatic monoamide analogues were partially reversible (see Fig. 18).

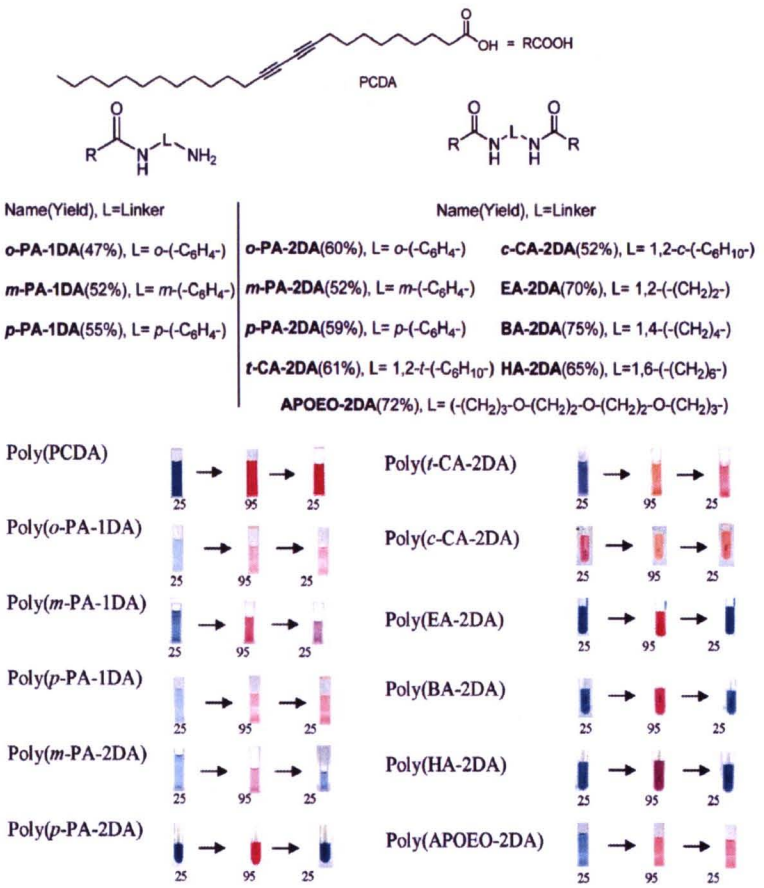

Figure 18 Structure of diamidodiacetylene monomers and thermochromic reversibility of the PDA sols illustrated by color photographs [22]

Scope of this research

In this study, we further investigate thermochromic properties of PDA assemblies prepared from various DA monomers, synthesized by S. Wascharasindhu and coworkers [22]. The structures of PDA assemblies are modified by varying chemical structures of the linker between the diamide groups. Different linkers including hydrophobic alkyl chain, phenyl group and hydrophilic ethyleneoxide chain are used. Moreover, the linkers are modified by increasing length of hydrophobic alkyl linker and varying the substituted position of phenyl linker. We investigate the effects of structural modification on thermochromic and fluorescence properties as well as morphologies of PDA assemblies in aqueous solutions and other solvents. We also study the reversible and irreversible thermochromism of PDA assemblies in various thin films. In addition, we investigate the effects of solvent on photo-polymerization of PDA assemblies and the effects of chain length on thermochromic properties.