CHAPTER III

RESEARCH METHODOLOGY

Monomers were supported from Organic Synthesis Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University and were synthesized as described in literature. [22] We investigate the effect of structural modification on thermochromic and fluorescence properties as well as morphologies of PDA assemblies in aqueous solutions and other solvents. In addition, we explore the reversible and irreversible thermochromism of PDA assemblies in various thin films.

Equipments

1. Differential Scanning Calorimeter (Mettler Toledo DSC1)
2. Scanning Electron Microscopy (SEM, LEO 1455 VP)
3. UV/vis spectrophotometer diode array (Analytik Jena Specord S100)
4. Luminescence spectrophotometer (Perkin Elmer Luminescence LS55)
5. Fourier transform infrared spectroscopy (Perkin Elmer Spectrum GX)
6. Pobe sonicator (SONICS Vibra cell)
7. Water bath sonicator (S70H Elmasonic)

Materials

1. N,N′-ethylenebispentacosa-10,12-diynamide monomer
2. N,N′-(butane-1,4-diyl)dipentacosa-10,12-diynamide monomer
3. N,N′-(pentane-1,5-diyl)dipentacosa-10,12-diynamide monomer
4. N,N′-(hexane-1,6-diyl)dipentacosa-10,12-diynamide monomer
5. N,N′-(3,3'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(propane-3,1diyl)) dipentacosa-10,12-diynamide monomer
6. N,N′-(1,4-phenylene)dipentacosa-10,12-diynamide monomer
7. N,N′-(1,3-phenylene)dipentacosa-10,12-diynamide monomer
8. N,N′-(1,2-phenylene)dipentacosa-10,12-diynamide monomer
9. Deionized water

10. Chlorofrom
11. Ethanol
12. 1-Butanol
13. 1-Hexanol
14. 1-Octanol
15. Hexane
16. Octane
17. Decane

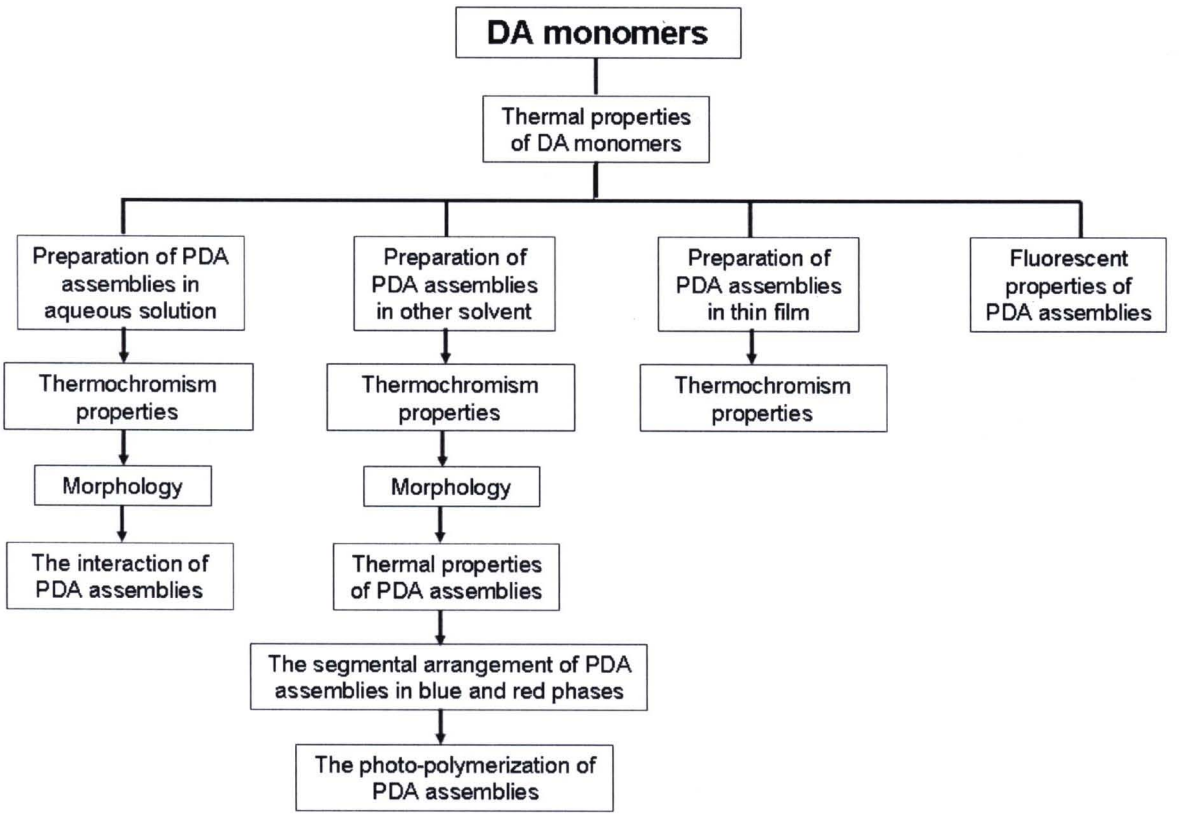

Figure 19 Flowchart of experiment

Methodology

1. Preparation of PDA assemblies in aqueous solutions

DA monomers were dissolved in chloroform and then filtered by using a 0.45 μm nylon filter to remove residual polymers. The solvent was removed by heating at ~60 °C. The deionized water was added to provide 0.5 mM aqueous suspension. The suspensions were heated to 75-85 °C, followed by water-bath sonication for 90 minutes to disperse DA monomers into aqueous medium. The suspension was allowed to cool down to room temperature and then kept at 4 °C for overnight. The solution was irradiated with UV light (10 W, λ~254 nm) for 2 minutes and filtered through 0.45 μm cellulose acetate membrane to remove large aggregates.

2. Preparation of PDA assemblies in other solvents

DA monomers were dissolved in chloroform and then filtered by using a 0.45 μm nylon filter to remove residual polymers. The solvent was removed by heating at ~60 °C. The solvent was added to provide 0.5 mM aqueous suspension. The suspensions were heated to 75-85 °C, followed by water-bath sonication for 30 minutes and probe sonication for 10 minutes to disperse DA monomers into solvent medium. The suspension was allowed to cool down to room temperature and then kept at 4 °C for overnight. The solution was irradiated with UV light (10W, λ~254 nm) for 2 minutes to give blue solution.

3. Preparation of PDA assemblies in thin films

The polymers used in this study include polyvinyl alcohol (PVA), polystyrene (PS) and polymethylmethacrylate (PMMA), The PDA assemblies in aqueous solution (0.5mM, 5 ml) were mixed with PVA (10%w/v, 5 ml). The solution was poured into a Petri dish (diameter 5 cm) and dried at 40 °C for 4 day. The blue color film was then peeled from dish. The PDA assemblies in ethanol and hexane are mixed with PMMA in chlorobenzene and PS in toluene (10%w/v), respectively. The solution mixed at ratio 1:1 v/v were dropped on quartz slide and dried at 40 °C for 4 day.

4. Thermal properties of DA monomers and PDA assemblies

Thermal properties of DA monomers and PDA assemblies are investigated by using Differential Scanning Calorimeter (DSC) (Mettler Toledo DSC1). All of

samples were purified by recrystallization process prior to the DSC measurement. About 3–5 mg of sample was encapsulated in aluminum pan and measured under nitrogen gas. The melting point was measured at peak temperature when heating from -10 °C to 210 °C and cooling from 210 °C to -10 °C for 2 cycles, using 5 °C/min heating and cooling rate.

5. Morphologies of PDA assemblies

The morphologies of the PDA assemblies were investigated by scanning electron microscopy (SEM, LEO 1455 VP). The samples for SEM measurements were prepared by dropping the PDA suspensions on polished silicon wafer.

6. Thermochromic and fluorescent properties of PDA assemblies

Absorption spectra of PDA vesicles were measured by using UV–vis spectrometer (Analytik Jena Specord S100) equipped with diode array detector and variable-temperature sample holder. In temperature-dependent experiments, the solutions were equilibrated at each temperature for 5 min prior to each measurement. The drop cast films and polymeric thin films are annealed for 5 minutes at different temperatures ranging from 30 to 250 °C. The photographs of PDA films at each temperature are recorded. When the films are cooled down to room temperature, the photographs and absorption spectra of the annealed film are measured to explore the color reversibility.

To quantify the extent of blue to red color-transition of PDA vesicles, the colorimetric response (%CR) was defined and calculated as follows:

$$\%CR = \left(\frac{PB_0 - PB}{PB_0} \right) \times 100$$

$$PB = \left(\frac{Absorbance_{blue}}{Absorbance_{red} + Absorbance_{blue}} \right)$$

The initial PB_0 value was determined before exposure to each stimulus.

The fluorescence properties of the PDA assemblies are investigated by Luminescence spectrometer, using excitation wavelength at 500 nm.

7. Preparation of PDA assemblies for infrared spectroscopy

The interaction of PDA assemblies is explored by utilizing infrared (IR) spectroscopy (Perkin Elmer Spectrum GX). The films were prepared by drop-casting on clean glass slides and dried in vacuum oven overnight. The films were measured in ATR mode.

The segmental arrangement of PDA assemblies in blue and red phases is explored by using KBr as a matrix. Powder of PDA assemblies were mixed with KBr and pressed into pellet for the measurement.