

CHAPTER V

CONCLUSIONS

In this study, we investigate the effect of structural modification on thermochromic and fluorescent properties as well as morphologies of PDA assemblies prepared in aqueous solutions and other solvents. In addition, we explore the reversible and irreversible thermochromism of PDA assemblies in various thin films. All of the results can be summarized as follows.

Thermochromic properties of PDA assemblies prepared in aqueous solutions

The variation of linkers affects both color transition temperature and the thermochromic reversibility. The color transition of alkyl linker with even number of carbon (N=2,4,6) occurs in a reversible fashion. The change to poly(PDPCDA-2DA) (N=5) and ethyleneoxide linker causes irreversible thermochromism. The color transition of PDA assemblies constituting phenyl linker, poly(p-PA-2DA) and (poly(c-CA-2DA)), also occurs irreversibly. However, the use of poly(m-PA-2DA) results in reversible color transition. The PDA assemblies in drop cast film exhibit higher color transition temperature than that of the solution form. The PDA assemblies exhibit two color transitions, including the reversible color transition at low temperature (blue to purple) and irreversible color transition at higher temperature (purple to red). The temperature range of complete reversible thermochromism varies with the linker. We also observe that the color transition temperature of PDA assemblies in this study is not related to the melting temperature of the corresponding monomers.

Thermochromic properties of PDA assemblies prepared in other solvents

The change from water to alcohol and alkane media results in PDA assemblies with higher molecular ordering. The SEM images clearly show well-define shape of sheet-like assemblies in alcohol and alkane. The increase of molecular ordering also yields PDA assemblies with longer conjugation length compared to that of aqueous system. In addition, the PDA assemblies in alcohols and alkanes exhibit higher color transition temperature. The color reversibility varies with types of solvent. The PDA

assemblies prepared in alcohols and alkanes exhibit partial reversibility, probably due to the penetration of the solvents into the outer layers of PDA assemblies during the heating process. The drop cast films obtained from alcohols and alkanes also exhibit three-step color transition which is different from PDA assemblies prepared in aqueous solutions. The color transition includes the 1st color transition from blue to purple, the 2nd color transition from purple to red and the 3rd transition from red to orange. The PDA assemblies prepared from all solvents exhibits the T_m at ~ 124 °C, which is close to the 2nd color transition temperature.

Effect of solvent on photo-polymerization of PDA assemblies

The photo-polymerization of DA assemblies exhibits different behaviors depending on type of solvent. In aqueous suspension, the λ_{max} value systematically decreases with the increase of the polymerization time, indicating the decrease of conjugation length. The photo-polymerization behaviors of DA assemblies in alcohols are rather different. In early stage, the increase of polymerization time causes slight decreases of the λ_{max} . Interestingly, further increasing of polymerization time results in an abrupt increase of λ_{max} . In the system of alkanes, the abrupt increase of λ_{max} upon increasing polymerization time is also observed. This result indicates that the difference of molecular ordering of DA monomers in various solvents causes the variation of chain ordering of resultant PDAs.

Effect of chain length on thermochromic properties

The increase of chain length affects the chain flexibility and ordering, which in turn cause the variation of color-transition behaviors of PDA assemblies. The chain length of PDA is varied by controlling the polymerization time. In aqueous suspension, the temperature of color transition decreases when the chain length is increased. The magnitude of color reversibility systematically decreases when the polymerization time is increased. For the alcohol and alkane systems, the increase of chain length also causes the decrease of color transition temperature. The magnitude of color reversibility, however, increases upon increasing polymerization time in early stage. Further increasing polymerization time leads to the decrease of magnitude of color reversibility similar to the aqueous system.

Thermochromic properties of PDA assemblies in polymeric thin films

We demonstrate that the PDA assemblies prepared in water, alcohol and alkane can be embedded in PVA, PMMA and PS matrices, respectively. The color transition behaviors of the PDA assemblies in these polymeric films are similar to those of the drop cast films, exhibiting two-step reversible and irreversible thermochromisms. The variation of polymeric matrices slightly affects the color transition behavior of PDA assemblies.

Fluorescence properties of PDA assemblies

The poly(PCDA), poly(APOEO-2DA) and poly(p-PA-2DA) assemblies in the red form exhibit fluorescent properties. The fluorescent intensity of all samples is rather weak. The spectra also exhibit different shape, which is probably due to the difference of molecular packing within the assemblies.