Preparation and thermochromic behaviors of polydiacetylene/indium or gallium doped zinc oxide nanocomposites

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Abstract. Polydiacetylene (PDA) is one of the well-known thermochromic materials having a high potential in applications such as displays and sensor technology. Many research groups have been working on controlling thermochromic reversibility of PDA-based materials. In this research, the colorimetric response of PDA assembled with indium or gallium doped zinc oxide was studied with various concentrations. Indium or gallium doped zinc oxide was prepared by hydrothermal method. The compositions of 5, 10, and 15% of indium and 5, 12, and 24% gallium, respectively. Undoped zinc oxide and gallium doped zinc oxide exhibited the nanoflowers composed of nanosheets while the indium doped zinc oxide showed the nanorod structure and combined to be nanoflowers. Monomer of PDA composing 10,12-pentacosadiynoic acid in ethanol was mixed with indium and gallium doped zinc oxide precursor solution at 20% weight. Ultra-violet light source was used to photo-polymerize for five minutes after incubation at low temperature for a prolong cooling. For nanocomposites of poly(PCDA) and undoped and gallium doped zinc oxide, the color of nanocomposite changed from blue to light-purple at above 70˚C and the color can be reversible when cooling down to room temperature. However, for nanocomposites of PCDA and indium doped zinc oxide, the color change from blue to light-purple at above 50˚C then become red than those in gallium doped PDA nanocomposite. In addition, the color of PCDA nanocomposite with indium doped zinc oxide cannot be reversible back to the original color.

1. Introduction
Polydiacetylene (PDA) is one of well-known conjugated polymers which has drawn enormous attention from various research groups in the past few decades [1,2]. It later became one of the most studied materials showing a blue to red color transition upon heating. The color transition of PDAs may vary upon the temperature range and their built-up structures. The conjugated backbones and side chain structures are taken into account for the color changes. Many research groups have been studied on the factors that affect the color transition range and thermochromic ability of PDAs. The aqueous suspension
incorporated with PDA assemblies can easily be prepared by monomers of 10,12-tricosadiynoic acid (PTDA) and 10,12-pentacosadiynoic acid (PCDA) which are commercially available. They showed the irreversible color transition of blue to red upon heating around 60°C [3].

The pure PDAs cannot be reversed to its original color upon cooling, however, the reversibility can be achieved by incorporating various types of cations and metal oxides which were investigated by several research groups [4-6]. These researches emphasized on interaction between the head groups and alkyl tails of PDAs, the electrostatic forces of PDAs and the substrate, the intercalation of the ions in bilayer structure affecting the thermochromic properties of PDAs, the photopolymerization time for tuning the reversibility of thermochromism of PCDA nanocomposites [3,7,8]. The reversible thermochromism have been extended for many applications [9-11].

The structure of PCDA can be modified by using various metal oxides such as zinc oxide (ZnO), titanium oxide (TiO$_2$), zirconium oxide (ZrO$_2$). The comparison between PCDA based on several nanocomposites had been investigated with the result of irreversible PCDA/TiO$_2$, PCDA/ZrO$_2$ and reversible PCDA/ZnO [12]. In this research work, the PCDA incorporated with hydrothermally synthesized nanoflower structures of indium or gallium doped zinc oxide were synthesized by hydrothermal method. The difference on the morphology of doped zinc oxide with various dopant percent was studied and compared. The synthesized indium or gallium doped nanoflowers were incorporated into PCDA assemblies and studied the thermochromic property especially reversibility and irreversibility properties of PCDA nanocomposite.

2. Experimental section

For synthesis of zinc oxide nanoflower and indium or gallium doped zinc oxide nanoflower, the precursors used are indium nitrate hydrate (In(NO$_3$)$_3$.xH$_2$O), gallium nitrate hydrate (Ga(NO$_3$)$_3$.xH$_2$O), zinc acetate dihydrate (Zn(CH$_3$COO)$_2$.2H$_2$O), sodium citrate dihydrate (C$_6$H$_5$Na$_3$O$_7$.2H$_2$O) and sodium hydroxide (NaOH). The chemicals were ordered from Sigma Aldrich without further purification. The solvent used is deionized water in all synthesis process.

In the synthesis of zinc oxide nanoflower, 0.1M of zinc acetate dihydrate was mixed with 0.24M of sodium citrate dihydrate in 30 ml of deionized water and magnetically stirred at 700 rpm and 40°C for 15mins. Then, 0.5M of sodium hydroxide was added to the precursor solution under vigorous stirring to form the white solution with precipitates. The solution was continuously stirred for 30 mins and hydrothermal synthesis was continued with the conditions of 120°C for 12 hours. The obtained solution was washed alternatively with deionized water and ethanol for 3 times by centrifugation at 4000rpm for 10mins. Then, the sample was dried in the oven under 60°C for 12 hours.

For the synthesis of indium or gallium doped zinc oxide, the total concentration of both indium and gallium doping synthesis was 0.1M. The doping of indium or gallium to zinc oxide was performed in three different percent ratios. For indium doped ZnO synthesis, the doping percentages of indium to zinc precursor were varied as 5%, 10% and 15%. For gallium doped ZnO, the doping percentages of gallium to zinc precursor were varied as 5%, 12% and 24%, respectively. The synthesis conditions as well as the hydrothermal conditions of indium or gallium doped zinc oxide nanoflowers were all the same as the synthesis of undoped zinc oxide nanoflowers.

For preparation of poly(PCDA)/ZnO based nanocomposites, the monomer used is 10,12-pentacosadiynoic acid (PCDA) and zinc oxide nanoparticles which are commercially available at Fluka and Nano Materials Technology (Thailand). The concentration of PDA monomers is prepared at 0.5 mM with the ZnO/PCDA ratio of 20wt %. The PDA monomer was dissolved in ethanol and sonicated for 5 min at room temperature. The obtained solution was filtered by 0.45 µm pore size nylon membrane to remove polymerized materials. Then ethanol was slowly evaporated around 45°C for about one and half hours.

The 20wt% zinc oxide nanoparticles were prepared by dissolving in 10 ml deionized water using sonicating probe for 10 min. After the ethanol dried up, the prepared zinc oxide precursor solution was added to the dried monomer beaker. The mixture between dried PDA monomers and zinc oxide suspension were sonicated around 75°C for one and half hours to allow the well dispersion of zinc oxide nanoparticles and monomers. Then the mixture was cooled down to room temperature and incubated at 4°C in refrigerator to allow the self-assembly of PCDA on surface of zinc oxide. The
photopolymerization was processed after 18 hours of incubation by exposing to the UV light with 254nm wavelength for 5 mins. The preparation route of other zinc-based materials such as zinc oxide nanoflowers, indium or gallium doped zinc oxide nanoflowers were conducted with the same protocol.

For used powder characterization, the morphology of undoped, indium or gallium doped zinc oxide nanoflower structures were investigated using Hitachi SU-8010 field emission scanning electron microscope. Thermochromism such as reversibility and irreversibility of PCDA/ZnO based nanocomposites were also studied starting from 30˚C to 90˚C by immersing the test tube containing the sample suspension in the beaker with hot water. Fourier transform infrared (FTIR) spectra were characterized for the comparison of carboxylate head groups of the prepared samples. Optical spectroscopy was also used for characterization of the absorption spectrum of the PCDA nanocomposite samples.

3. Results and discussion
The morphologies of the hierarchical undoped zinc oxide nanoflowers and indium or gallium doped zinc oxide nanoflowers can be observed by SEM images. From the SEM images of undoped zinc oxide nanoflowers, the particles have uniform distribution as shown in figure 1(a). The average diameter of the nanoflowers is about 2.7µm which composed of stacking nanosheet structures.

![SEM images of prepared nanoflower structures of (a) undoped zinc oxide, (b) 15% indium doped zinc oxide and (c) 12% gallium doped zinc oxide.](image)

In the case of indium doped zinc oxide nanoflowers, the nanoflower particles are uniformly distributed at low dopant percent and the nanoflower with nanorod like structures is formed at high dopant percent. The nanoflower with small needle-like rods can be observed at 5% indium doped ZnO, as shown in figure 1(b). When the dopant percent was brought to 10% and 15%, the nanorods distributed more however the aggregated form can be seen under high magnification. This obviously showed that the indium doped nanoflower is composed of hexagonal nanorods.

In contrast to indium doped zinc oxide nanoflowers, the gallium doped zinc oxide nanoflowers were found to be in more round plate shape like structure and cannot observe spine nanoflower form, as shown in figure 1(c). According to high magnification image, the formation of round nanoflower composes of the stacking of flat plate nanosheets. The thickness of the nanosheets were found out to be about 52nm.

Thermal reversibility and irreversibility of poly(PCDA)/ZnO based materials suspension were investigated from 30˚C to 90˚C. The aqueous containing PCDA/indium or gallium doped zinc oxide suspensions in the test tubes were immersed into the heated water beaker with the heating step of 10˚C and measured and photographed. The color change of the poly(PCDA)/ZnO based materials can visually be illustrated in figure 2 corresponding with the temperature increment. The blue-to-purple color transition can be observed at about 70˚C and 80˚C in all doped samples except poly(PCDA)/InZnO (In:ZnO = 15:85). The original blue color can be regained by cooling down to room temperature as indicating for complete thermochromic reversibility for poly(PCDA)/ZnO (also agree with the previous work [7]) and poly(PCDA)/GaZnO, however the poly(PCDA)/InZnO nanocomposite with the highest percent doped of indium to zinc oxide exhibited thermochromic irreversibility. The increasing amount of doping concentration for gallium or indium doped in PCDA provides increasing of the transition
temperature except highest percent doped of indium to zinc oxide. The numerical values of CIE 1931 xy coordinates measured at room temperature before and after heating the samples up to 90°C are described in table 1. The xy coordinates are approximately the same for all samples except poly(PCDA)/InZnO (In:ZnO = 15:85) indicating the incomplete thermochromic reversibility.

Table 1. CIE 1931 xy coordinates before and after temperature test.

| Sample                  | (x, y) coordinates before temperature test | (x, y) coordinates after temperature test |
|-------------------------|--------------------------------------------|-------------------------------------------|
| poly(PCDA)/ZnO nfs      | 0.441501, 0.38211                           | 0.44592, 0.38936                           |
| poly(PCDA)/GaZnO (Ga:ZnO = 5:95) | 0.445645, 0.388592                     | 0.446429, 0.388864                     |
| poly(PCDA)/GaZnO (Ga:ZnO = 12:88) | 0.438703, 0.380073                       | 0.410727, 0.375523                       |
| poly(PCDA)/GaZnO (Ga:ZnO = 24:76) | 0.429408, 0.374891                       | 0.424938, 0.374625                       |
| poly(PCDA)/InZnO (In:ZnO = 10:90) | 0.438207, 0.38403                        | 0.435632, 0.383156                        |
| poly(PCDA)/InZnO (In:ZnO = 15:85) | 0.419571, 0.388229                       | 0.341685, 0.362177                       |

The blue to purple transition of poly(PCDA)/InZnO (In:ZnO = 15:85) occurs around 50°C and the color at 90°C shows reddish rather than purple. However, when it is cooled down to room temperature, the color can reverse to only the color observed around 55°C. This indicated incomplete thermochromic reversibility as shown in figure 3. The color components of each sample is different according to the type of zinc oxide-based material and absorption spectra of each sample were investigated for further examination of the color reversibility of poly(PCDA)/indium or gallium doped zinc oxide nanocomposites.

As mentioned above, PDA nanocomposites are well-known for a wide range of applications especially in sensor industry because of their thermochromic reversibility and suitable application can be selected according to the requirements whether it shows complete thermochromic reversibility or not. In this work of comparison among PDA incorporated with different zinc oxide nanoflower precursors, poly(PCDA)/InZnO (In:ZnO = 15:85) was highlighted out with figure 3 as it behaves differently with only partial reversibility, which is similar to the results when PCDA was incorporated with ZrO₂ and TiO₂[12].

Figure 2. Color photographs of PCDA/gallium and indium doped zinc oxide nanocomposites at temperature of 30, 40, …, 90°C.
Figure 3. Incomplete thermochromic reversibility of poly(PCDA)/InZnO nanocomposite with the 15:85 ratio of In:ZnO.

Optical absorption spectrum was analyzed at room temperature before and after the thermochromic test up to 90°C. The spectra of poly(PCDA)/ZnO nanocomposites and various poly(PCDA)/indium or gallium doped zinc oxide nanocomposites were measured to compare. Another broad shoulder appears at ~675 nm. All the spectra of poly(PCDA)/ZnO based materials nanocomposites show similar spectra with approximately the same absorption wavelength as shown in figure 4(a). According to the spectra analyzed after the thermochromic test, almost of spectra do not deviate from their original spectra except that for poly(PCDA)/InZnO (In:ZnO = 15:85) as seen in figure 4(b). It shows two broad peaks at ~500nm and ~538nm indicating the partial thermochromic reversibility, this is in agree with the results of color photographs.

According to the FTIR spectra shown in figure 5, the peaks appearing at 2848, 2918, and 2954 cm\(^{-1}\) shows the presence of PCDA vesicles [6]. Carboxylate groups with no interaction was also found in all nanocomposite samples according to the peak at 1720cm\(^{-1}\). The significant difference found is the appearance of shoulder before the peak of 1720cm\(^{-1}\) for poly(PCDA)/indium doped zinc oxide nanocomposite samples which was not found as compared to the previous work of PCDA incorporated with various zinc precursors [6]. Though these shoulders have not been assigned to any specific groups of interaction, an assumption of being difference to other samples likewise the difference found in morphology of indium doped zinc oxide nanoflowers.
Figure 4. Optical absorption spectra of various aqueous suspension poly(PCDA)/indium and gallium doped ZnO nanocomposites at room temperature (a) before and (b) after thermochromic test.

Figure 5. FT-IR spectra of (a) around the shoulder of carboxylate with no interaction and (b) peak poly(PCDA)/indium or gallium doped zinc oxide nanocomposites.
4. Conclusion
In this work, nanoflower structures of synthesized of undoped, indium or gallium doped zinc oxide nanoflower structures were illustrated by SEM images with different nanoflower morphologies. By using these nanoflower materials, the thermochromic modification to poly(PCDA) has been performed and analyzed. According to the analyzed results, the indium doped zinc oxide nanoflower which is composed of hexagonal rod like structure has modify effects on incomplete thermochromic reversibility when incorporated into poly(PCDA) suspensions. The difference of the property of the sample from the rest can be noticed by their FTIR and optical absorption spectra after thermochromic test at 90°C.

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