

Thermochromic reversibility of conjugated polymers derived from a diacetylenic lipid containing lithium salt

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Polydiacetylenes derived from self-assembled diacetylenes containing lithium salt are found to display a very rapid thermochromic reversibility.

Polydiacetylene (PDA) based sensors have attracted unprecedented attention over the past decade owing to their applications in detection of a wide range of analytes. PDAs obtained by the topotactic polymerisation of diacetylenes (DAs) are π -conjugated polymers that display impressive optical and electrical properties. These properties are exploited well in the design of sensors that respond with a blue to red colour change under the influence of various stimuli like heat, organic solvents, mechanical stress and ligand-receptor interactions.¹

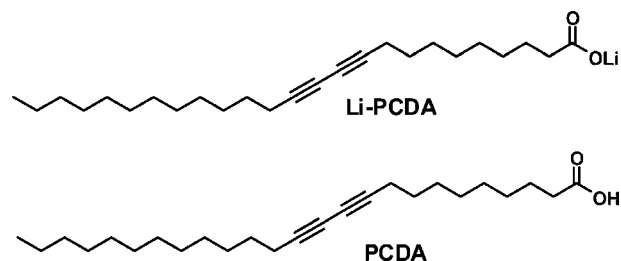
DA supramolecular aggregates have been obtained in the form of liposomes/vesicles,² micelles,³ Langmuir-Blodgett/Langmuir-Schaefer films,⁴ nano-wires,⁵ nano-tubes,⁶ and nano-fibers;⁷ all of which are amenable to facile photo polymerisation. A literature review reveals that chromism in polymerised DA nanostructures reported thus far is largely irreversible, *i.e.*, there is only a one-way blue-to-red colour change under the influence of an external stimulus. This irreversible chromism has caused limitations in their applications as sensors and “on-off-on” switches. However, in our group, we have been concentrating our efforts towards designing reversible PDA-based sensors, the properties of which can be readily tuned. Consequently, we reported earlier *via* a series of articles that enhanced intermolecular interactions among the head groups in PDAs confer them with reversible thermochromism.^{4a,8} We accomplished this by preparing a large number of 10,12-pentacosadiynoic acid (PCDA) derivatives incorporating specific functional groups which enhanced the bonding among the head groups in the adjacent monomers. In addition to our research group, some other articles in recent times have also reported on the reversible colorimetric transition in these aggregates based on a similar principle of enhanced bonding.⁹ In PCDA hybrids based on mesoporous silica¹⁰ and layered double hydroxides,¹¹ reversible thermochromism was realised by covalent/noncovalent bonding of PDA head groups to the inorganic moieties. Despite all the effort put into this issue, there still leaves a lot to be explained with regards to the exact mechanism of the colour change.

In keeping with our continuing interest in PDA chromism, we present here the reversible thermochromism displayed by PDA derived from the lithium salt of 10,12-pentacosadiynoic acid (referred to as Li-PCDA henceforth). The structures of Li-PCDA and PCDA are shown in Scheme 1. Until now Li-PCDA was used as a radiochromic film manufactured under the trade name Gafchromic EBT.

In one of the earliest investigations of the EBT film, it was found to be about eight times more sensitive to an ionizing radiation dose compared to a film made of PCDA.¹² Our experimentation revealed, much to our surprise, a complete colorimetric reversibility in the Li-PCDA derived PDA supramolecules as can be seen in what follows.

The Li-PCDA salt was prepared as reported earlier.¹³ Briefly, purified PCDA (0.112 g, 0.3 mmol) was dissolved in an aqueous solution of tetra ethyl ammonium hydroxide (0.221 g, 1.5 mmol) and the solution was stirred for about 4 h at 60 °C. An aqueous solution of lithium acetate (0.037 g, 0.3 mmol) was injected into this hot solution, and further stirred for about an hour at the same temperature. The resulting homogeneous solution was cooled to room temperature to facilitate crystallisation, and finally refrigerated for about 4 h. The Li-PCDA salt thus obtained was found to be extremely sensitive to UV treatment. The colourless Li-PCDA dry salt generated a brilliant blue colour upon UV irradiation (*ca.* 1 mW cm⁻²) for a mere one second. PCDA however displayed a very slight colour change (colourless to pale blue) for an identical irradiation time. Similar to the dry salt, a suspension containing Li-PCDA was far more UV-sensitive than a suspension of PCDA liposomes. The former generated a deep blue coloured solution within one second of UV irradiation, while the latter could reach a similar shade of blue only after a 30 s irradiation. These colour changes are depicted in Fig. 1. The generated blue colour in the samples can be explained on the basis of polymerisation of the DA monomers with the formation of conjugated ene-yne polymer backbone, which is the hallmark of PDAs.

The marked difference in the varying shades of blue obtained upon irradiation could be dependent on the crystal structures of the two salts. It is known that the three-dimensional structure and packing of DA monomer crystals depends on the type and size of side groups.^{14,15} It is thus reasonable to suggest that the crystal structure modification brought about by the replacement of H⁺ by Li⁺ should be responsible for the observations here. Furthermore, it has been observed in PCDA Langmuir-Blodgett films that there is a change in



Scheme 1 Molecular structures of Li-PCDA and PCDA.

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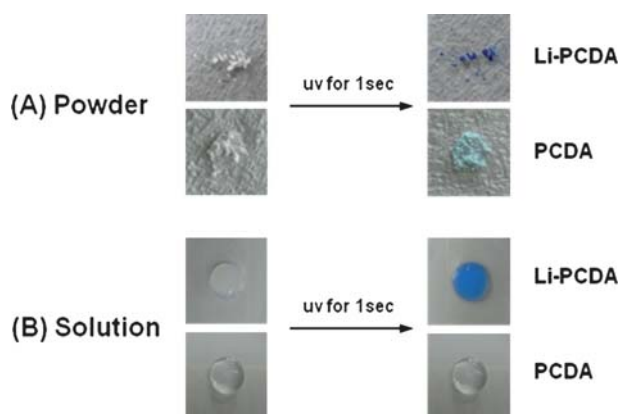


Fig. 1 Photographs depicting the effect of UV irradiation on Li-PCDA and PCDA dry salts (A) and solutions (B).

the polymer crystal structure with increased radiation dose, which is manifested as a shift in absorbance maximum.¹⁶ The underlying chemistry in this absorbance shift is an increase in distance between the last polymer unit and the next available monomer, resulting in a decrease in the rate of polymerisation. A visual manifestation of a decreased polymerisation rate would be a pale blue salt/solution. Following this argument a little further, we highlight the observations of Rink *et al.*, which state that there is no shift in absorption maximum observed in a Li-PCDA based film when it is irradiated with an X-ray beam for about 240 s.¹² This was taken to suggest that the internal packing of the monomeric Li-PCDA crystals is more stable than the PCDA crystals, and that there should be little or no separation between the monomer and polymer structures. This lead the authors to propose that there should be no significant decrease in the rate of polymerisation in the Li salt, unlike in PCDA. This rationalisation holds well in our observations *vis-à-vis* the generation of deep blue salt and solution of Li-PCDA with a mere one second UV irradiation (1 mW cm^{-2}).

The SEM images of Li-PCDA shown in Fig. 2 are symptomatic of a stick-like morphology. These augur well with the observations of Rink *et al.* for the EBT film.¹² Part (B) of the figure shows spherical liposome structures for the PCDA counterpart.

The most impressive feature observed in the Li-PCDA salt is its rapid reversible thermochromism. We noted that the polymerised Li-PCDA salt displays a pinkish-red colour immediately after heating. These crystals revert to their deep blue colour within a minute of cooling the sample, passing through different shades of pink and blue. This finding attains importance because the polymerised

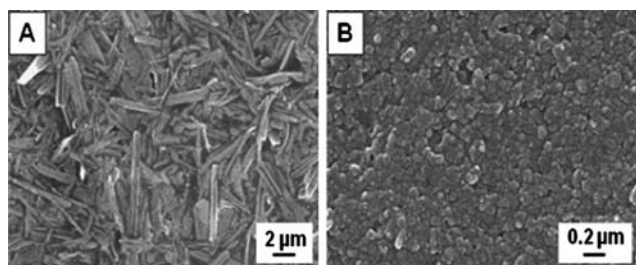


Fig. 2 SEM images of Li-PCDA (A) and PCDA (B) samples at room temperature.

acid-PCDA salt does not display this reversible thermochromism. This may well be attributed to the difference in the strengths of interaction of Li^+ and H^+ with the carboxylate oxygens. The enhanced intermolecular interactions in the case of the Li salt, confer the PDA with the observed reversible thermochromism, much similar to that seen in the sodium-PCDA salt.¹⁷ It may be recalled at this stage that much of our earlier work and that from other groups concerning chromatic reversibility was based on modifications in DA monomers to enhance bonding among the head groups. This included every conceivable mode of bonding starting from the introduction of multiple hydrogen bonding, stronger aromatic interactions, better ionic interactions, and also the consideration of covalent bonds in the monomers. In the light of the foregoing information, it thus makes sense to suggest that enhanced intermolecular interactions in Li-PCDA leads to a recovery of the conjugation length of the π -electron chromophore after the cooling process following the thermal stimulation of the polymer.

We additionally investigated thermochromic changes in Li-PCDA and PCDA embedded polyvinyl alcohol (PVA) films. This was done by mixing either a Li-PCDA solution (*ca.* 3 mM, 5 mL) or a PCDA liposome solution (*ca.* 3 mM, 5 mL) with 10 w% PVA in water (5 mL; 1 : 1, vol%), after which the solution was poured into a petri dish (diameter 6.5 cm). After drying for 5 days at room temperature, the generated film was peeled off and cut into squares with sides measuring 1.8 cm. Just like the dry salt, the Li-PCDA embedded PVA film developed a deep blue colour within just a second of UV light irradiation. Further illumination rendered the film a deep navy blue. The PCDA embedded PVA film, however, didn't show any colour change within a second of UV irradiation, and required irradiation for about 5 min to attain a blue colour.

The thermal treatment of these PVA embedded films displayed some interesting results. The Li salt based film was found to display reversible thermochromism, such that the UV irradiated navy blue film changed to red upon heating to 130 °C. The film was found to display thermal stability up to 140 °C. Upon removal of the heat source, the red film gradually retraced its colour trajectory back to navy blue, as shown in Fig. 3. When subjected to an identical heat treatment, the PCDA liposome embedded PVA film, changed to red at 90 °C, and upon further heating, attained an orange hue (beyond 100 °C). Cooling this film did not produce any colour change, thus

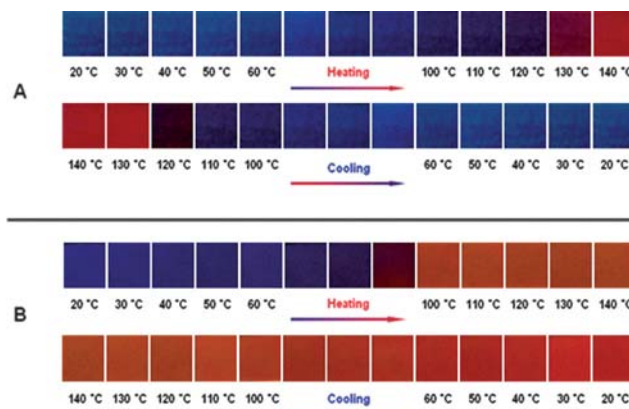


Fig. 3 Photographs of Li-PCDA solution (A) and PCDA liposome (B) embedded PVA films at different temperatures. Photographs were taken after 1 min of incubation at each temperature.

confirming that thermochromism in PCDA liposome embedded PVA film is irreversible.

It is generally accepted that colorimetric transitions in PDAs result from changes in the effective conjugation length of the polymer backbone in response to various external stimuli. There is a wide consensus that if the backbones can restore their original conformation after the removal of the stimulus they display a red-to-blue colorimetric reversibility. In earlier reports dealing with this concept it was found that the conformational changes in the backbones were substantially dependent on the structure and position of the head groups. Consequently, the colorimetric reversibility when observed either for the parent carboxylic acid polymer or other related derivatives was never as rapid as seen in the case of Li-PCDA.

In conclusion, we have reported here on the thermochromic reversibility of a novel PCDA, namely its lithium salt, Li-PCDA. Based on our investigation, we summarise the differences between the Li salt and the parent polymer as follows: (i) the dry salt, solution, and PVA based films of Li-PCDA display an extremely rapid development of brilliant/deep blue colour upon UV irradiation for a mere one second. The PCDA counterparts could attain only a pale blue colour with one second of irradiation. (ii) The second and more prominent difference between the two polymers is in their thermochromic behaviour. The Li-PCDA solution and films in a PVA matrix display a fast red-to-blue thermochromic reversibility, while the parent acid based samples are thermochromically irreversible. The parent acid based samples are thermochromically irreversible. With these impressive properties and the ease of its synthesis, it wouldn't be inappropriate to term Li-PCDA *sui generis*.

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