



High temperature thermochromic polydiacetylene supported on polyacrylonitrile nanofibers

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ABSTRACT

Polydiacetylene (PDA) are polymers known to switch from blue to red when exposed to environmental stimuli. This paper reports on electrospun composite nanofibers of polyacrylonitrile (PAN) and a high temperature PDA. The effect of PAN on the thermal and thermochromic properties of the PDA was studied. PDA to PAN mass ratio in the composites was varied and an unusually high loading of 30 wt% PDA was achieved. Scanning and transmission electron microscopies (SEM, TEM) revealed a randomly-packed morphology of nanofibers with well dispersed PDA particles inside. Through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), the heat resistant PAN nanofibers were found to increase the reversible temperature range of the embedded PDA while also improving its thermal stability. Naked eye observations suggested that the composite thermochromic sensor can be reversed from temperatures around 200 °C - a big improvement from just 156 °C - while ultraviolet–visible spectroscopy (UV–vis) studies showed that there was a progressive deterioration of the conjugated PDA backbone which ultimately resulted in complete loss of reversibility and colorimetric character at 230 °C.

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1. Introduction

Polydiacetylenes (PDAs) are emerging as promising tools for visual detection and monitoring of chemical, biological and physical targets. This is due to their sensitivity to environmental perturbations, to which they respond by changing their emission properties. PDAs belong to a class of polymers known as conjugated polymers, which have interesting properties due to their ability to form polymer chains with extensive conjugation. This extensive conjugation enables conjugated polymers with properties that can be exploited to design functional materials for various applications. For example, conjugated polymers have been exploited in the manufacture of and applications requiring conducting materials [1–3], highly electro-magnetic composites [4], and materials with enhanced photocatalytic activity [5,6], to name a few.

The most striking property of PDAs as conjugated polymers, however, is their optical properties. Typically, PDAs undergo a blue-

to-red colour transition once their ene-yne conjugated backbone is distorted by exposure to a stimulus [7]. This unique feature has led many research efforts to design PDA molecules with detection or monitoring abilities for specific stimuli. Common PDA stimuli include, among others - metal ions [8,9], organic solvents [10,11], pH [12–15], biochemical compounds [14,16,17] and heat [18–23]. Temperature monitoring is among the most investigated PDA stimuli, probably due to the fact that all PDAs, regardless of the targeted stimulus, can be affected by temperature depending on the amount of heat it is subjected to [24].

In the past, reversible thermochromism was one of the most desired features for PDAs until methods were developed to achieve reversibility, which were primarily based on extensive hydrogen bonding [25–29], and metal ion interaction [30–32]. Hydrogen bonding is the most common method and many studies have demonstrated that hydrogen bonding amongst head group atoms results in higher reversibility temperature ranges, and that has been the basis of the design of high temperature reversible thermochromic PDAs. In a recent study, our work involved the use of urea as a modifier to a diacetylene (DA) to introduce reversibility and raise possible operation temperatures [23]. In addition to these,

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the newly synthesised PDA was able to exhibit several distinctive chromatic transitions within its reversible range which could be used as colorimetric signals for reporting temperature. Most reported PDAs lack the feature of several clearly distinctive chromatic transitions.

In many cases, however, PDAs are transformed into thin films or nano/microfibers to make them easier to use or handle compared to powder and vesicle forms [18,22,33,34]. The urea-based PDA reported recently [23] was insoluble in common solvents and thus could not be transformed from a powder into a film or nanofibers for better handling. The disadvantage of powders is that a relatively big amount of the material may be required in order to make one sensor unit, which may be costly. In some literature, PDA has been embedded into polymer nanofibers via electrospinning [14,20,35], or into cast films [20,21]. Basically, electrospinning involves application of electrostatic potential to a polymer to discharge a thin jet that stretches and thins into very narrow filaments called nanofibers that randomly collect on a grounded metallic surface to form a mat. Compared to thin films, electrospun nanofibers have enhanced specific surface area and high porosity, which makes them attractive materials for manufacturing of ultrasensitive sensors for various applications [20].

In this regard, the limit to the use of nanofibers as substrates is how much additive can be accommodated without disturbing the continuous electrospinning and morphology of the composite. The capacity of a polymer solution towards the additive should, therefore, be taken into consideration when choosing a suitable substrate. Moreover, the choice of a substrate should be influenced by the required properties of a polymer in relation to the intended application. For high temperature thermochromic nanofibers, one would desire that just like the embedded PDA, the substrate can withstand high temperatures so as not to compromise the performance of the PDA.

Visibility is also a key factor for PDAs because their essence is the ability to colorimetrically report the detection of stimuli. This can be easily missed if the choice of polymeric substrate is such that continuous electrospinning to form nanofibers can only be achieved with very low amounts of additive. This would be expected of a polymer whose optimum electrospinning parameters include high solution concentration, which directly translates to a highly viscous solution [36]. Upon further addition of content to such a solution, clogging may occur, effectively stopping the process [37]. To summarise the discussion above, high temperature thermochromic nanofibers should be most suitably electrospun from a temperature-resistant polymer and one whose solution has a high capacity for PDA additive, i.e. a polymer that can be electrospun at relatively low concentration (viscosity).

Studies have shown PAN to be electrospinnable at low concentrations, giving uniform and defect-free nanofibers [36,38,39]. Furthermore, PAN nanofibers loaded with up to 35 wt% (with respect to the mass of PAN) multiwall carbon nanotubes (MWCNTs), which is a relatively high loading for a powder additive, have been reported [40], which highlights the high capacity of PAN nanofibers as substrates. PAN has also been shown to resist temperature as high as 220 °C before it undergoes cyclisation prior to carbonisation in the process of preparing carbon nanofibers [40–42]. These observations and properties suggest that PAN nanofibers would be a suitable substrate for a high temperature PDA thermochromic sensor.

In this contribution, the effect of PAN nanofibers on the thermal and thermochromic properties of PDA is investigated. PAN nanofibers embedded with newly synthesised pcd-urea, a PCDA derivative with a urea head group, were used as thermochromic sensors. Although we demonstrated previously that pcd-urea powders can be used as high temperature thermochromic sensors, the

disadvantages associated with powders can limit the usage of the thermochromic sensor. After giving consideration to the criteria of a suitable polymer matrix for high temperature PDA thermochromism, PAN was selected as a model polymer. To the best of our knowledge, PAN nanofibers have not been used as a matrix for thermochromic PDA. PAN nanofibers acting as supports for the PDA are expected to provide better portability (ease of handling). In addition, the enhanced surface area and dispersive ability of nanofibers can be expected to reduce the amount of PDA powder required to produce a unit of the sensor. The significance and contribution of this work was to show how – other than performing chemical modification of PDA – other polymers with related properties to that of the PDA could be exploited to manipulate the properties of the PDA.

2. Experimental section

2.1. Materials and reagents

Polyacrylonitrile (PAN, average $M_w = 150\,000$) was purchased from Aldrich, Germany. N,N-Dimethylformamide anhydrous (DMF, 99.8%), 10,12-pentacosadiynoic acid (PCDA, 97%, HPLC), oxalyl chloride (reagent plus, >99%) and urea (ACS reagent, 99.0–100.5%) were purchased from Sigma-Aldrich, Germany. Dichloromethane (DCM, 99.5%, GC) and Pyridine (99.5%, GC) were products of Associated Chemical Enterprise (ACE), South Africa.

2.2. Synthesis of pcd-urea

The method from our previous study [23] for the preparation of pcd-urea, which was adopted from Ji et al. [43] with modifications, was followed. In brief, PCDA (1.0 g) was dissolved in 20 mL DCM and the prepolymerised portion was filtered off through a 0.45 μm PTFE syringe filter. The PCDA solution was transferred to a 100 mL round bottom flask before adding 0.5 mL oxalyl chloride and stirring at room temperature. After 2 h, a drop of DMF was added to the mixture to catalyse the reaction to completion for a further 2 h, followed by concentrating under reduce pressure. The concentrate was added drop wise to a flask containing urea powder (0.15 g) dispersed in 20 mL DCM and pyridine (0.2 mL). This reaction was allowed to stand for 20 h under stirring at room temperature, following which it was filtered and washed first with DCM and then lukewarm water before drying in oven at 30 °C.

2.3. Electrospinning of nanofiber composites

Electrospinning mixtures were prepared by first dispersing pcd-urea in DMF under sonication for 5 min. Then PAN was added to make a PAN concentration of 10% (w/v), which was kept constant in all mixtures. The mass ratio of PAN to pcd-urea in the mixtures was varied at 10:0, 10:1, 10:2 and 10:3. The mixtures were stirred overnight (~16 h) in darkness before loading into a plastic syringe attached to a blunt stainless steel needle and electrospinning. An electrospinning setup consisting mainly of a high voltage direct current and a programmable syringe pump (New Era Pump Systems® NE-1000, USA) was used to generate nanofiber composites at 12.5 kV, 15 cm between the tip and the collector, and 0.6 mL/h flow rate. A grounded aluminium foil was used as a collector. The nanofibers were dried in an oven in the dark at 60 °C for 24 h prior to illumination with UV₂₅₄ light (Spectroline E-Series ENF-240C/FE UV lamp) for 2 min, 3 cm above nanofibers surface.

2.4. Measurement

A mixture of potassium bromide and sample was pressed into a

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