Abstract. Emulsified diacylenes as reporter molecules in micelle gel dosimeters were evaluated in the current article. It was observed that gels containing PCDA emulsified in deionized water using SDS changed from colourless to blue upon irradiation. Unfortunately, recipes that led to turbid gels resulted in a colour change, but transparent gels did not change colour. The colour change may be due to the oligomerization of precipitated solid PCA crystals, rather than emulsified PCDA.

1. Introduction

New radiochromic micelle gel dosimeters [1] for optical readout were recently developed by Jordan and coworkers [2-4]. These dosimeters consist of colourless leuco-dyes emulsified in a hydrogel matrix using a surfactant. The leuco-dye molecules react with free radicals, generated by water radiolysis, and change from colourless to deeply coloured as the radiation dose increases.

Micelles are self-assembled aggregates of surfactant molecules that have both hydrophilic and hydrophobic parts. Above the critical micelle concentration (CMC), surfactant molecules orient themselves so that their hydrophobic parts are at the centres of the micelles and their hydrophilic parts are in contact with water. The main purpose of using micelles in radiochromic micelle gel dosimeters is to emulsify water-insoluble reporter molecules to distribute them throughout the gel volume [2]. Micelles are significantly larger than individual reporter molecules. As a result, the micelles have low diffusivity within the gel matrix, which improved the spatial stability of dose information, compared with micelle-free optical dosimeters such as Fricke gel dosimeters [3]. A key benefit of dosimeters that display changes in optical properties is that they can be read out using optical CT rather than MRI, which is expensive and unavailable in many locations [4-6]. Optical CT scanners are low in cost, and could be readily accessible in most clinical environments [7, 8].

Micelle gels (mainly composed of water) should be more tissue equivalent than competing plastic (e.g., PRESAGE) dosimeters [4]. Moreover, the simplicity of fabricating water-based dosimeters, as opposed to polyurethane-based PRESAGE dosimeters, gives considerable advantages to micelle gels for use in anthropomorphic phantoms [4]. Current micelle gel dosimeters could benefit from further improvements as they are light-sensitive and temperature-sensitive during irradiation and tend to fade over time [2]. They also have a relatively low dose sensitivity and may have significant dose-rate dependence [3].

In an attempt to develop improved micelle gel dosimeters, the use of emulsified diacylenes, especially PCDA (see Fig. 1), as reporter molecules is investigated in this paper. PCDA molecules are
the reporter molecules used in radiochromic GafChromic® films which are widely used for 2D dosimetry [9, 10]. Diacetylenes are organic molecules that contain two conjugated acetylene groups [10]. Upon irradiation, diacetylene molecules can react to give polymers that have conjugated double and triple bonds, which result in formation of colour, with intensity that is proportional to the absorbed dose [10, 11]. Diacetylenes other than PCDA have also been used as reporter molecules in self-developing films [12]. Figure 1 shows the three diacetylenes considered in this study, along with their melting points. Note that these diacetylenes are solids at room temperature.

**Figure 1:** Chemical structure of some diacetylenes with their Molecular weight and melting point.

## 2. Materials and methods

### 2.1. Preliminary experiments

Preliminary experiments focused on emulsifying PCDA (GFS chemicals, Ohio, USA) using three different common surfactants at different concentrations. The three surfactants (Fisher Scientific, Ottawa Canada) are the anionic surfactant Sodium Dodecyl Sulfate (SDS), the nonionic surfactant Triton x-100, and the cationic surfactant Cetyl Trimethyl Ammonium Bromide (CTAB). All were dissolved in deionized water. A variety of concentrations for both the PCDA and the surfactants were tested as shown in table 1. Bovine gelatin (300 Bloom bovine bone, Eastman Gelatin Corp., MA, USA) [13] was added to make the gels. All emulsions and gels were manufactured by first preparing stock solutions of surfactants then adding the monomer, and stirring at 58 °C for 15 minutes. Mixtures were then heated to slightly above the melting point of the monomer and stirred for 15 minutes until the emulsion was clear. The mixtures were cooled to room temperature then gelatin was added and left to swell for 30 minutes. Mixtures were then stirred at 45 °C until they became clear. All samples were then refrigerated at 4 °C. Samples of the prepared emulsions and gels were irradiated 48 h after manufacturing to 100 Gy (Varian Clinac 6EX, 400 MU/min, 10x10 cm² field size). This large dose was used so that any oxygen inhibition would be unimportant.

**Table 1:** Transparent solutions and gels manufactured for preliminary testing.

| Vial # | PCDA Conc. | Surfactant Type | Surfactant Conc. | Gelatin Added | Irradiated |
|-------|------------|----------------|------------------|---------------|------------|
| 1     | 3 mM       | SDS            | 51 mM            | 0 wt%         | Y          |
| 2     | 3 mM       | SDS            | 51 mM            | 0 wt%         | N          |
| 3     | 3 mM       | SDS            | 51 mM            | 5 wt%         | Y          |
| 4     | 3 mM       | SDS            | 51 mM            | 5 wt%         | N          |
| 5     | 16 mM      | SDS            | 327 mM           | 0 wt%         | Y          |
| 6     | 16 mM      | SDS            | 327 mM           | 0 wt%         | N          |
| 7     | 16 mM      | SDS            | 327 mM           | 5 wt%         | Y          |
| 8     | 16 mM      | SDS            | 327 mM           | 5 wt%         | N          |
| 9     | 8 mM       | Tx-100         | 60 mM            | 0 wt%         | Y          |
| 10    | 8 mM       | Tx-100         | 60 mM            | 0 wt%         | N          |
| 11    | 8 mM       | Tx-100         | 60 mM            | 5 wt%         | Y          |
| 12    | 8 mM       | Tx-100         | 60 mM            | 5 wt%         | N          |
| 13    | 5 mM       | CTAB           | 54 mM            | 0 wt%         | Y          |
| 14    | 5 mM       | CTAB           | 54 mM            | 0 wt%         | N          |
| 15    | 5 mM       | CTAB           | 54 mM            | 5 wt%         | Y          |
| 16    | 5 mM       | CTAB           | 54 mM            | 5 wt%         | N          |
2.2. Experiments comparing PCDA and other diacetylenes
The three diacetylenes in figure 1 were emulsified in SDS using the procedure above. Gels of PCDA, DPBD (Aldrich) and HD (Aldrich) were prepared using overall reporter concentrations of 3 mM in emulsions containing 51 mM SDS. Bovine gelatin was added at 5 wt%. Samples of the prepared gels were irradiated 24 h after manufacturing to 0, 5, 10, 20 and 40 Gy. Spectra of irradiated samples containing PCDA were measured using a SpectroVis Plus spectrophotometer (Vernier Software & Technology, OR, USA). In addition, PCDA gels from different batches were replicated (manufactured and irradiated) 10 times using 3 mM PCDA and 10 Gy.

2.3. Gel ageing and phase behaviour experiments
PCDA gels with concentrations 3 and 9 mM were prepared using 5 wt% gelatin and 51 mM SDS. Gel samples were irradiated to 10 Gy at the following times after manufacturing: 0.5, 1.5, 2.5, 3.5 and 7.5d.

3. Results and Discussion
Figure 2 shows a photograph of non-irradiated and irradiated vials (two hours after irradiation) from the experiments in table 1. Vials containing CTAB did not show any noticeable colour change. SDS and Triton x-100 vials, with and without gelatin, turned blue in response to radiation. Irradiated vials containing SDS showed deeper blue colour compared to those containing Triton x-100. Note that the samples that showed colour change are cloudy. Based on these preliminary experiments, the next set of experiments focused on emulsions containing various diacetylenes using SDS as the emulsifier.

![Figure 2: Irradiated and non-irradiated vials containing emulsions and gels from table 1 irradiated to 100 Gy. The symbol G indicates vials containing gelatin.](image)

During the second set of experiments, vials containing DPBD and HD did not change colour in response to irradiation. Vials containing PCDA (Fig. 3) showed a smooth response to radiation, with no apparent threshold that would indicate oxygen inhibition (Fig. 3c) [14, 15]. This type of response occurred in three of the 10 replicated experiments. In seven trials, no colour change was observed, indicating poor reproducibility. Note that all vials that exhibited a colour change were turbid before irradiation. Vials that remained clear during the 24 h period between manufacturing and irradiation did not change colour.

Gel aging experiments were designed to further investigate whether the colour change was related to turbidity (i.e., oligomerization of precipitated PCDA). The goal was to track gel clarity over time and to check whether colour change occurs only in precipitated PCDA gels, or whether it could also occur in PCDA micelles (transparent gels). The two PCDA gels (3 mM and 9 mM) remained clear during the first 24 h after manufacturing, and the 9 mM PCDA gel showed some cloudiness after 1.5 d. The 3 mM PCDA gel started to become cloudy about 2.5 days after manufacturing. Turbidity increased with time for both PCDA concentrations. Figure 4 shows the absorbance (at 670 nm) for vials of PCDA gels irradiated to 10 Gy at different times. Note that gels that were transparent showed no colour change. Turbid gels turned blue during irradiation and the colour intensity was higher for
gels that were more turbid. Also, the colour intensity was higher for the 9 mM gel samples than for the 3 mM samples, presumably due to a larger amount of precipitated PCDA in the 9 mM gels.

![Image](image1.png)

**Figure 3:** Response of PCDA (3 mM) gel with SDS (51 mM) to 0, 5, 10, 20, and 40 Gy doses, irradiated 24 h after manufacturing. The figure shows a) a photograph of the vials immediately after irradiation, b) measured spectra for these vials and c) absorbance at 680 nm for the irradiated vials from two experiments. Of the 10 replicate experiments, only three showed a colour change in response to irradiation.

![Image](image2.png)

**Figure 4:** Absorbance at 670 nm of PCDA gels (3 mM and 9 mM) emulsified in SDS at 51 mM irradiated to 10 Gy. The absorbance of the 9 mM PCDA gel is higher than that for the 3 mM gel indicating more PCDA precipitation.

4. Conclusions

The use of emulsified diacetylenes as reporter molecules in micelle gel dosimeters was evaluated. Many gels containing PCDA changed from colourless to blue upon irradiation. For the emulsifier concentrations tested, the colour was deeper when PCDA gels were prepared using SDS than using Triton x-100. Gels produced using CTAB remained clear and did not show any colour change due to radiation. Gels containing SDS and the other diacetylenes (DPBD and HD) did not show any colour change upon irradiation. The response of gels containing PCDA and SDS to irradiation was smooth with no apparent dose threshold that would indicate oxygen inhibition.

Throughout the experiments, only turbid gels changed colour in response to irradiation. When samples of transparent gels were aged, resulting in PCDA precipitation over a period of days, the cloudy PCDA gels changed colour in response to irradiation. These results indicate that the colour change is due to oligomerization of solid PCDA particles, rather than oligomerization of PCDA in micelles. Since PCDA crystallization is not very reproducible and turbid gels are undesirable for
optical CT readout, the use of emulsified diacetylenes for three-dimensional gel dosimetry does not seem to be promising.

5. References
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