



Short communication

# Photonic polymer multilayers for colorimetric radiation sensing

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## ABSTRACT

We introduce a new approach for colorimetric sensing of ionizing radiation based on photonic polymer multilayer films. Upon immersion in a solvent, the multilayers give rise to reflected structural color in the visible region of the spectrum, with a coloration that depends on the degree of swelling of the low-index layers. Exposure to ionizing radiation leads to either preferential degradation or crosslinking of the low-index polymer, yielding a change in color in the swelled state. We demonstrate the operation of both red- and blue-shifting colorimetric sensors, with sensitivity to electron-beam irradiation in the range of ~100 kGy, and also show that this approach allows for the preparation of sensors on flexible plastic substrates.

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## 1. Introduction

The ability to conveniently sense ionizing radiation is critical for a variety of applications including in medicine, defense, industrial food packaging, and pasteurization and sterilization techniques. Practical ranges for absorbed dose detection vary from the range of 1 Gy and below for human exposure, to upwards of hundreds of kGy for sterilization and decontamination procedures [1]. Colorimetric sensors are convenient and can offer both simple and accurate read-out. Many such detection techniques, however, rely on a change in optical density triggered by irradiation of a photo-sensitive chromophore and require external equipment for read-out in addition to stringent storage conditions to avoid device failure [2]. Some solution-based sensors which show clear colorimetric changes spanning a broader range of the visible spectrum provide an attractive means towards convenient, stand-alone sensors, but utilize inconvenient and toxic organic solvents [3–5]. Among the many existing approaches, film-based sensing techniques are appealing for general use because they avoid potentially toxic solvents, however may also require sealed containment or have time-sensitive restrictions on read-out due to a lack of chemical stability post-irradiation [6–9].

Here, we report a novel concept for radiation detection via colorimetric photonic sensing. We make use of devices based on

one-dimensional photonic crystals, periodic multilayer structures that rely on the interference of light to reflect a characteristic wavelength defined by the refractive index and thickness of each layer [10]. One-dimensional photonic sensors have been explored extensively for detection of a wide range of analytes, including pH, ionic strength, temperature and a variety of small molecules, as summarized in several recent reviews [11–13]. Previously, our group has developed an approach to photonic multilayers for colorimetric temperature sensing based on photo-crosslinkable polymers [14]. This simple fabrication method is broadly suitable for a wide range of photonic sensors, including chemical and biological analytes, and in the current report we explore the extension to a new type of analyte, ionizing radiation.

We demonstrate that these multilayer polymer films provide a novel platform for radiation sensing, due to the radiation-induced preferential crosslinking or dislinking of a swellable polymer gel layer within the photonic sensor. This allows for straightforward colorimetric read-out, and due to the reliance on changes in structural color, rather than absorption or emission of light by a chromophore, offers potential for the development of low cost and chemically stable radiation sensors.

## 2. Materials and methods

### 2.1. Polymer synthesis

Polymers were synthesized by conventional free radical polymerization using azobisisobutyronitrile (AIBN) (Aldrich) recrystallized from methanol as initiator. Acrylamidobenzophenone (BP) monomer was synthesized according to a previously reported

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literature procedure via reaction of acryloyl chloride and 4-aminobenzophenone [15].

### 2.1.1. P(*p*-MS-BP)

Inhibitor was removed from *p*-methylstyrene (*p*-MS) (Acros Organics) by passing through a column of basic alumina. The monomers *p*-MS (3 mL, Aldrich) and BP (0.45 g) were polymerized in 30 mL of 1,4-dioxane at 80 °C for 15 h under nitrogen following three freeze–pump–thaw cycles, resulting in a copolymer containing 10 mol% of BP. The polymer was purified by precipitation into methanol, washed under vacuum filtration and dried overnight in a vacuum oven prior to use. Structure was confirmed by <sup>1</sup>H NMR (Bruker DPX 300).

### 2.1.2. P(OEGMA-BP)

Amounts of 2 mL of 2-(2-methoxyethoxy) ethyl methacrylate (MEO<sub>2</sub>MA, Aldrich), 251 μL of oligoethylene glycol methyl ether methacrylate (OEGMA, *M<sub>n</sub>* = 475 g/mol, Aldrich), 58 mg of BP and 3.4 mg of AIBN were polymerized in a 5:1 mixture of ethanol:1,4-dioxane at 80 °C for 18 h under nitrogen following three freeze–pump–thaw cycles, resulting in a copolymer containing 2 mol% of BP. OEGMA and MEO<sub>2</sub>MA were used as received. The polymer was purified by dialysis and lyophilization, and its structure confirmed by <sup>1</sup>H NMR.

### 2.1.3. P(MMA-BP)

Amounts of 2 g (20 mmol) of methyl methacrylate (MMA) (Sigma, purified via 3 × sat. sodium bicarbonate washes followed by drying over sodium sulfate), 0.25 g (1 mmol) of acrylamide benzophenone, 8.2 mg (0.05 mmol) of AIBN (recrystallized from methanol) were dissolved in 10 mL of 1,4-dioxane and sparged with N<sub>2</sub> for 30 min before heating to 85 °C. The reaction was allowed to stir for 48 h and purified by precipitation into methanol, resulting in a polymer containing 5 mol% BP by <sup>1</sup>H NMR.

## 2.2. Sensor preparation and characterization

Photonic multilayers were prepared by sequential spin-coating, crosslinking and developing of polymer films as previously reported [14]. Glass substrates were first cleaned by sonication for 10 min each in acetone, ethanol and water followed by surface treatment with methacryloxypropyl trichlorosilane (Gelest) to promote substrate–polymer adhesion. Flexible Mylar substrates (McMaster-Carr) were used as received and cleaned by rinsing with water, acetone and ethanol. P(*p*-MS-BP) and P(OEGMA-BP) were cast from toluene, while P(MMA-BP) was cast from cyclohexanone. Developing solutions for the three respective copolymers were 1:0.65 toluene:hexanes, 1:0.53 toluene:hexanes, and chloroform. Polymer films were crosslinked using a Newport 365 nm UV light source, with a typical dose of approximately 80 J/cm<sup>2</sup>, which is sufficient to fully convert the BP photo-crosslinkers. A Magellan 400 scanning electron microscope was used for all radiation exposure. As-prepared multilayers were exposed to electron beam radiation by scanning a 1 mm × 1 mm square at 150× magnification with fixed accelerating voltage of 15 kV, and current of 1.6 nA. At 15 kV, the excitation volume depth for all three polymers is in the micrometer range. Therefore, we can assume that all layers are excited and the electron beam penetrates the entire thickness of the multilayer sensors, which are ≈0.5 μm in total thickness. The radiation dose was varied by adjusting exposure time *t*, and was quantified in terms of the approximate absorbed dose according to:

$$\text{dose} \approx \frac{I \times S \times t}{A} \quad (1)$$

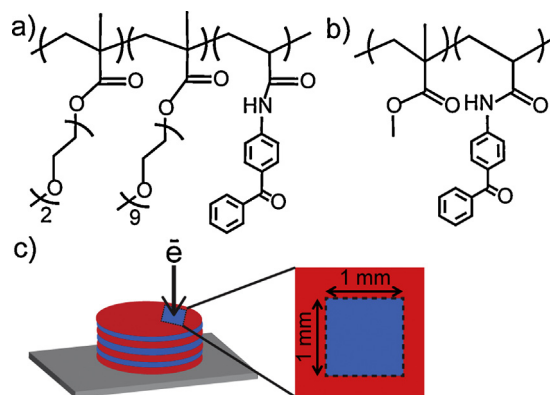
where *I* is the current, *S* the stopping power, and *A* the exposure area. Values for stopping power for 15 keV kinetic energy electrons were calculated using the NIST ESTAR database based on the chemical compositions of the polymers, yielding an average value for P(*p*-MS-BP), P(OEGMA-BP) and P(MMA-BP) of 16 MeV cm<sup>2</sup>/g, which was used to estimate absorbed doses [16].

The response of irradiated samples was determined by swelling in ethanol and acquiring reflectance spectra *in situ* using a reflectance probe (Semiconsoft MProbe) integrated with an upright microscope (Zeiss Axiotech). The microscope aperture was adjusted to ensure that the measured area fell entirely within the irradiated square.

## 3. Results and discussion

Our approach to colorimetric radiation sensors is based on one dimensional photonic multilayers fabricated by spin-coating, photo-crosslinking, and developing of alternating layers of a high refractive index polymer, P(*p*-MS-BP) and one of two different low refractive index polymers. The layer thicknesses were chosen to reflect blue–violet light in the dry state and undergo a red-shift due to swelling of the low refractive index layers upon immersion in a mild, non-toxic solvent (in this case, ethanol). Depending on their chemical structure, polymers tend to undergo either preferential crosslinking or degradation under ionizing radiation [16]. Thus, upon irradiation of the multilayers, the degree of swelling of the irradiated regions will either increase or decrease, depending on the chemical structure of the low-index layers, thereby causing a shift in the reflectance peak compared to the unexposed regions of the sample. Once irradiated and immersed in ethanol, the color change can be monitored by eye. Depending on the chemistry of the responsive polymer layers, the observer will note an apparent red- or blue-shift of the irradiated region compared to the non-irradiated area of the sensor. This shift can be more quantitatively monitored by using a reflectance probe to measure the reflectance spectra of the irradiated and non-irradiated regions. Once read-out is complete, the sensor can be dried and disposed of or re-used by exposing a previously non-irradiated region of the sample.

Two radiation sensor systems were designed based on polymers expected to undergo radiation-induced crosslinking or degradation, respectively, P(OEGMA-BP), Fig. 1a, and P(MMA-BP), Fig. 1b. The materials were copolymerized with 2–5 mol% of the photo-crosslinkable monomer BP to allow for UV crosslinking during multilayer fabrication. Mid-chain carbon-centered radicals on poly(ethylene oxide) (PEO) irradiated *in vacuo* are known to predominantly undergo crosslinking via radical recombination,



**Fig. 1.** Chemical structures of responsive materials (a) P(OEGMA-BP) and (b) P(MMA-BP) and (c) schematic of multilayer radiation exposure setup and dimensions.

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