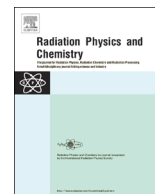




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# Polymer-gel formation and reformation on irradiation of tertiary-butyl acrylate

Tiantian Yao, Antonia G. Denkova, John M. Warman\*

Delft University of Technology, Reactor Institute Delft, Department of Radiation and Isotopes for Health, Mekelweg 15, 2629 JB DELFT, The Netherlands

## HIGHLIGHTS

- Gamma-ray polymerization of tertiary-butyl acrylate; dose and dose-rate dependences of monomer conversion.
- The radiolytic production of a rigid, UV/vis transparent organic gel.
- Primary radiolytic processes relevant to the preparation and application of a radio-fluorogenic polymer-gel.
- Reformation of an organic polymer gel by swelling subsequent to removal of monomer by evacuation.

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## ABSTRACT

The purpose of the present research was to provide a radiation-chemical basis for the use of tertiary-butyl acrylate gels in radio-fluorogenic dose-imaging applications (Warman et al. 2011a,b, 2013a,b). The radiation-induced polymerization of tertiary-butyl acrylate (TBA) results in the formation of a transparent gel with an optical density lower than  $0.1 \text{ cm}^{-1}$  from 600 nm down to 315 nm. The fractional monomer-to-polymer conversion,  $C_M$ , determined gravimetrically, increases super-linearly with dose,  $D$  Gy. Up to  $C_M \approx 40\%$ , and over the dose rate range  $D' = 3.5$  to  $49 \text{ cGy s}^{-1}$ , the dose dependence is given by  $C_M = [1 + AC_M]KD/\sqrt{D'}$  with  $K = 1.43 \times 10^{-3} \text{ Gy}^{-0.5} \text{ s}^{-0.5}$  and  $A = 0.70$ . For  $D' = 3.5 \text{ cGy s}^{-1}$  the average polymer size is estimated to be  $1.2 \times 10^5$  monomer units or 17 megadalton. For  $C_M \geq 10\%$  the gel is quasi-rigid, displaying little tendency to flow on a timescale of an hour or more. After removal of monomer by evacuation, the gel can be reformed by adding a volume of monomer to the remaining polymer equal to that removed and allowing this to swell for several days. The dose and dose rate dependence of radiation-induced monomer conversion in the reformed gel show no evidence of a discontinuity caused by the intervening evacuation and reformation procedures.

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## 1. Introduction

In their pioneering paper Day and Stein (1950) said “In the search for a suitable system which would enable three-dimensional distributions of absorbed energy to be demonstrated, we have experimented with gels containing dyes which are reduced with change of color on irradiation”. The gel matrix in their study functioned to limit the free diffusion of chromophoric radiolytic products, resulting in their (at least temporary) spatial fixation in the location where they were formed. This idea has been the basis of most subsequent attempts to produce physico-chemical-based, 3D radiation dosimeters (Baldock 2006; Jirasek 2006; McAuley 2006; Baldock et al. 2010; Schreiner et al. 2010). Until recently only aqueous gels have been used with natural

polymers such as gelatin or agarose forming the gel matrix. Invariably two or more additional chemical components are included in order to induce the particular radiogenic effect to be probed and related to the dose deposition. The great variety and chemical complexity of gel recipes proposed can be found in the recent reviews of the topic given above. There is little doubt that this complexity, and the associated difficulty of assuring an (internationally) consistent composition and quality of the chemicals used (including the water!), presents one of the barriers holding back the general clinical adoption of the polymer-gel method of 3D dosimetry.

We have recently demonstrated the ability of a chemically simpler, two-component gel recipe to produce three-dimensional images of the dose distribution produced by a variety of radiation sources including collimated X-ray beams (Warman et al. 2011a), an Ir-192 brachytherapy seed (Warman et al. 2011b), and electron (Warman et al. 2013a) and proton (Warman et al. 2013b) particle beams. The method is based on the radiation-induced, free-radical

\* Corresponding author. Tel.: +31 152786115.

E-mail address: [J.M.Warman@TUDelft.NL](mailto:J.M.Warman@TUDelft.NL) (J.M. Warman).

polymerization of a bulk monomer (tertiary-butyl acrylate, TBA) and the co-polymerization of a second monomer component (maleimido-pyrene, MPy) present in low (*ca* 100 ppm) concentration. The *non-fluorescent* MPy is converted into the *fluorescent* succinimido derivative, -SPy-, on incorporation into the poly-TBA chain. In this way the medium develops a fluorescent intensity in ultraviolet light that is proportional to the yield of free-radicals formed by the radiation and hence to the dose deposited (Warman et al. 2009a,b). As shown in Warman et al. 2011b, the method is capable of ready, real-time imaging of complex dose distributions without the necessity of expensive and not-readily-available diagnostic techniques.

In order to prevent diffusion of the fluorescent polymer chains from their point of formation, their motion is restricted by a 3D polymer-gel network, as in other polymer-gel dosimeters. In our case however the overall gel (network *plus* encapsulated monomer) consists for 99.99% of a single chemical component, *i.e.* partially (*ca* 15%) polymerized and cross-linked tertiary-butyl acrylate; a major component in many over-the-counter hair-styling gels. An initially non-fluorescent form of the radio-fluorogenic gel (RFG) is prepared by a process of: irradiation of pure TBA to *ca* 15% monomer conversion; removal of remaining monomer by evacuation; addition of an equal volume of a dilute solution of MPy in TBA to the remaining polymer; swelling of the polymer back to its original gel form and consistency. This somewhat tedious procedure is necessary because straightforward formation of a gel by irradiation of an MPy solution directly would result in a gel with an initial high background fluorescence over its whole volume.

Because of the dominance of TBA polymerization in both the passive gel formation procedure and the active dosimetric co-polymerization process, we decided to carry out a thorough study of the radiation chemistry of TBA with particular attention given to the dependence of monomer-to-polymer conversion on accumulated dose and dose rate, and the reproducibility of the radiation-chemical properties after a gel reformation procedure. The work presented here concerns therefore only pure TBA. In future studies the present results will be related to monomer conversion and fluorescence studies on RFGs containing MPy.

## 2. Experimental

### 2.1. Materials

The radiation-polymerizable monomer investigated in this work was tertiary-butyl acrylate, TBA (Sigma-Aldrich >98%, #327182); a colorless liquid with the elemental composition C<sub>7</sub>H<sub>12</sub>O<sub>2</sub> and molecular weight 128.2 g mol<sup>-1</sup>. As supplied the liquid contains *ca* 20 ppm hydroquinone stabilizer. This was removed by passage over an inhibitor removal column (Sigma-Aldrich #306312) after which the liquid was stored in glass vessels, in the dark, at 5 °C. The density of the liquid at 20 °C is 0.89 kg L<sup>-1</sup> corresponding to a monomer concentration of 6.94 mol L<sup>-1</sup>. The density of fully-polymerized TBA resin is 1.09 kg L<sup>-1</sup>. For a fractional monomer-to-polymer conversion C<sub>M</sub> the density will be approximated by:

$$\rho(C_M) = [0.89(1 - C_M) + 1.09C_M] \text{ kg L}^{-1} \quad (1)$$

For C<sub>M</sub> = 15%,  $\rho = 0.92 \text{ kg L}^{-1}$ .

Other properties of TBA relevant to the procedures used here are the boiling point, 120 °C, and the room temperature vapor pressure, 16 mbar. The former needs to be reasonably high to prevent evaporation of large amounts of monomer during de-aeration by purging with nitrogen. On the other hand, the vapor pressure

should be high enough that removal of the remaining monomer by evacuation after polymerization does not require an excessively long time.

Note: TBA is non-explosive but flammable and precautions should be taken to ensure good ventilation of the vapor during handling. It is also aggressive towards many plastics and should be contained only in glass or polyethylene vessels. General information on health and safety precautions when handling TBA are readily available (Material Safety Data Sheet, [http://www.chemicalbook.com/CASEN\\_1663-39-4.htm#MaterialSafetyDataSheetMSDS](http://www.chemicalbook.com/CASEN_1663-39-4.htm#MaterialSafetyDataSheetMSDS))

Testament to the lack of serious health hazards; TBA is widely used as a copolymer in over-the-counter hair-styling gels.

### 2.2. Sample preparation

Approximately 100 mL TBA in a glass flask was pre-purged with nitrogen in a fume hood for *ca* 2 min prior to placing the closed flask in the transfer compartment of a glove box (PLAS LABS model GB 818). Several coded and weighed sample containers were transferred open, together with the closed TBA flask into the glove box. The sample containers used for the gravimetric measurements of monomer conversion were 20 mL glass "liquid scintillation vials" (LSVs) with metal-foil-lined polypropylene screwcaps. The LSVs and TBA container were allowed to stand for at least 24 h in the glove box, which was continuously flushed, 24/7/52, with nitrogen, to remove any traces of oxygen on the surfaces of the vessels. The TBA was then purged with nitrogen in the glove box for 30 min after which 10 mL aliquots were pipetted into each LSV. These were then closed and placed in the glove-box transfer compartment.

For optical absorption measurements, a square, 10 × 10 mm<sup>2</sup> (internal dimensions) quartz glass cell fitted with a GL14 screwcap was used. This could be placed in the cell holder of a UV/vis spectrophotometer (Kontron Uvikon-940). For these measurements a 3.5 mL aliquot of de-aerated TBA was used.

### 2.3. Irradiation procedure and monomer conversion

The LSVs containing 10 mL de-aerated TBA were placed in the irradiation chamber of a GC200 (Atomic Energy of Canada) or a GC220 (Nordion) gamma-ray source with dose rates of *ca* 3.5 or 49 cGy s<sup>-1</sup> (*ca* 2.0 or 30 Gy min<sup>-1</sup>) respectively. The precise dose rates on the day of irradiation were based on Fricke dosimetry corrected for the 2778 day exponential decay time (5.27 yr half-life) of cobalt-60.

The fractional monomer conversion, C<sub>M</sub>, after a given dose D Gy was determined gravimetrically: after irradiation the LSVs were opened and weighed prior to being placed in a vacuum oven (Heraeus) at room temperature. The remaining monomer was removed by evacuation using a diaphragm pump. At regular intervals the LSVs were removed from the oven, weighed and replaced. From this the fraction of monomer plus polymeric TBA remaining *h* hours after the start of evacuation, W(*h*)/W(0), was determined. Some representative data for different doses are plotted in Fig. 1 for an evacuation period of approximately 2 weeks (336 h).

For doses up to *ca* 20 Gy a constant plateau value of W(*h*)/W(0) was reached within a week (168 h) of beginning evacuation. For doses in excess of 20 Gy the time required to reach a plateau value increased substantially. This can be associated with the formation of a complete 3D gel network that restricts monomer motion to the surface and hence retards evacuation. For such samples the weighing procedure was extended until the weight loss over an intervening period of two days was less than 2%. The value of C<sub>M</sub> was taken to be equal to the ultimate plateau value of W(*h*)/W(0), *i.e.* C<sub>M</sub> = W(∞)/W(0).

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