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Radiation-chemical and optical properties of a radio-fluorogenic gel

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Abstract. The radiation-induced polymerization and fluorescence intensity of a radiofluorogenic medium consisting of tertiary-butyl acrylate (TBA) with ca 100 ppm maleimidopyrene (MPy) display a super-linear dependence on dose and a close to inverse square root dependence on dose rate over the range from 2 to 30 Gy/min. In contrast with the fluorescence, the clarity and optical absorption remain unchanged on irradiation up to at least 17% monomer conversion for which the medium is a rigid gel.

1. Introduction

A radio-fluorogenic (RFG) gel becomes fluorescent in UV light after exposure to high-energy radiation. This radiation-induced fluorescent property is *permanent*, which distinguishes it from transitory optical emission or scintillation effects. We have shown that a quasi-rigid RFG gel, consisting of tertiary-butyl acrylate (TBA) with *ca* 100 ppm maleimido-pyrene (MPy), can be used to make fixed fluorescent images of complex radiation fields, including those produced by overlapping X-ray beams [1], 3MeV electrons [2], 80 MeV protons [3] and an Ir-192 brachytherapy seed [4]. In the last case we demonstrated that RFG images could be video-recorded in situ during seed insertion and retraction. Having shown *qualitatively* the potential of a TBA/MPy gel to produce spatially resolved images of dose deposition, we have initiated a programme of research into the fundamental radiation chemistry and photophysics of the medium with the ultimate goal of providing a *quantitative* fluorescence-based method of *in-situ* 3D dosimetry. The work presented here is a follow-up to a preliminary investigation of the dose and dose-rate dependence of polymer-gel formation on irradiation of pure TBA [5].

2. Experimental

The radio-fluorogenic medium studied here consists of >99% TBA, a monomeric acrylate that rapidly polymerizes when exposed to high-energy radiation, and *ca* 100 ppm of the fluorogenic compound MPy. MPy is initially non-fluorescent but becomes fluorescent when incorporated into a growing chain of TBA. Both compounds are commercially available and inexpensive. Details on material suppliers and physical properties are to be found in [1]. All samples were de-aerated prior to irradiation and prepared in a nitrogen-flushed glove box. Two cobalt-60 gamma-ray sources were used to irradiate samples: a GC200, dose rate ca 2 Gy/min and a GC220, dose rate ca 30 Gy/min. The actual dose rate on the measurement days was corrected for the natural decay of cobalt-60.

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The fractional conversion of monomer to polymer was determined gravimetrically by weighing irradiated samples before and after vacuum evacuation of remaining monomer, as described in [5]. For monitoring optical properties, the samples were contained in 1 cm square screw-capped, borosilicate glass cuvettes, and irradiated as described in the next section. The optical absorptive and emissive properties of the samples were monitored using a Kontron Instruments UV/vis spectro-photometer and an Ocean Optics fibre-optic spectro-fluorimeter with LED excitation at 365 nm.

3. Results and Discussion

3.1. Monomer to polymer conversion, C_M

In figure 1 the fractional conversion of monomer to polymer is plotted as a function of dose for pure TBA and for a 0.6×10^{-3} mol/L (*ca* 100 ppm) solution of MPy in TBA. The data were obtained using the GC200 and GC220 sources with dose rates differing by a factor of approximately 15. For free-radical chain-polymerization with chain termination controlled by second order radical-radical combination and disproportionation, C_M is expected to be a linear function of dose, D, divided by the square root of the dose rate, D'. This behaviour is approached for low values of C_M as shown by the dashed lines in figure 1. An increasing positive deviation from linearity is however apparent. This super-linear dependence can be described by the relationship $C_M = K_C.a/(1 - Ba)$ with $a = D/\sqrt{D'}$ [5]. The full-line fit to the pure TBA data in figure 1A was calculated using values of $K_C = 0.143 \text{ Gy}^{-0.5} \text{ s}^{-0.5}$ (for C_M in %) [5]. The same values were used to calculate the full line in figure 1B. As can be seen the fit to the high dose rate data for the MPy solution is good indicating that the presence of 100 ppm MPy does not significantly influence the polymerization kinetics. At the lower dose rate the C_M values are slightly lower than the fit line. This may be due to a small contribution from a first-order chain termination reaction that becomes more important at lower doses for which the free-radicals live longer.



Figure 1. The dependence of the monomer-to-polymer conversion, C_M , on accumulated dose normalized by the square-root of the dose rate for A, pure TBA and B, a *ca* 0.6×10^{-3} mol/L solution of MPy in TBA. Open and closed symbols correspond to dose rates of *ca* 2 Gy/min and *ca* 30 Gy/min respectively. See the text for the calculation of the full and dashed lines.

3.2. Optical absorption and emission spectra

In figure 2 are shown the optical absorption spectra of a saturated solution of MPy in TBA (*ca* 1.8×10^{-3} mol/L) before irradiation and after a GC200 dose of 20 Gy. For this dose the medium has changed from a free-flowing liquid to a rigid gel that shows little tendency to flow on a timescale of an hour or more [5]. Also, 17% of the monomer has been converted to polymer with an average chain length on the order of 10^{5} monomer units. After irradiation the gel remains as clear as the original solution with no indication of the creation of additional absorptions or turbidity. This independence of

the absorptive and light-scattering properties of an RFG gel on dose is particularly relevant to the interpretation of 3D images since it means that one can take the attenuation with depth of the UV excitation light and the self-absorption of the emitted fluorescence within the medium to be constant and uniform.



Figure 2. Circle and cross data points: the optical density of a 1.8×10^{-3} mol/L solution of MPy in TBA before and after irradiation with a dose of *ca* 20 Gy respectively. Line spectra: the fluorescent emission of a 0.6×10^{-3} mol/L solution of MPy in TBA before irradiation (dotted line) and after doses of 8 Gy (dashed line) and 16 Gy (full line).

In contrast to the optical absorption, the fluorescent emission changes dramatically on irradiation, from close to zero initially, to a readily measureable, blue emission after only a few Gy. This is due to the fact that the S_0 to S_1 absorptive transition of MPy is controlled mainly by the aromatic pyrene moiety, which remains unchanged on co-polymerization, while the S_1 to S_0 emissive transition is controlled by the maleimido moiety, which changes dramatically on co-polymerization to a succinimido moiety, which no longer quenches the normal pyrene fluorescence.

3.3. Dose and dose rate dependence of the fluorescence

In figure 3 the intensity of the fluorescence at the spectral maximum (395 nm) is plotted against D/\sqrt{D}' for a 0.6×10^{-3} mol/L MPy solution. The data display a similar dependence to that shown in figure 1**B** for the monomer-to-polymer conversion. The full line drawn in figure 3 is a best fit to the high dose rate data using the relationship I = K_I.a/(1 - Ba). The value of B, which describes the upward curvature of the data, was fixed to that used in figure 1, *i.e.* 1.00×10^{-3} Gy^{-0.5}s^{-0.5}. The fluorescence is seen to follow the same super-linear behaviour as found for the monomer conversion. As for the C_M measurements for the solution, the values for the lower dose rate tend to be somewhat lower than for the high dose rate. An investigation of the dependence of the fluorescence on MPy concentration is presently underway in order to clarify a possible secondary influence of MPy on the polymerization kinetics.



Figure 3. The intensity at 395 nm of the fluorescent emission of a 0.6×10^{-3} mol/L solution of MPy in TBA as a function of the accumulated dose normalized by the square-root of the dose rate. Open and closed symbols for dose rates of *ca* 2 Gy/min and *ca* 30 Gy/min respectively. For the calculation of the full and dashed lines see the text.

4. Conclusions

We have shown that the radiation-induced polymerization of tertiary-butyl acrylate results in a dependence of the monomer-to-polymer conversion, C_M (%), on dose, D (Gy), and dose rate, D' (Gy/s), of the form $C_M = 0.143D/\sqrt{D'}/[1 - 0.001D/\sqrt{D'}]$ for $C_M 30\%$ or less and dose rates from *ca* 0.03 to *ca* 0.5 Gy/s. From the value of C_M after irradiation of TBA for a time t at a dose rate D', the actual value of the dose rate can be determined from D' = $[C_M/(0.143 + 0.001C_M)t]^2$.

We have also shown that the intensity of the radiation-induced fluorescence of TBA containing a low concentration of the fluorogenic compound MPy parallels closely the dose dependence of C_M . Making fixed fluorescent images of complex radiation fields in the quasi-rigid gel state of TBA ($C_M > 10\%$ [5]) under exactly the same conditions of UV excitation as for homogeneously irradiated, gamma-ray calibration samples should make it possible to determine the local dose rate. Parallel research is also being carried out on radio-chromic films, which are close to dose rate independent, with a view to combining the two methods, both of which have sub-millimetre spatial resolution.

For quantitative measurements corrections for absorption of the excitation light and the emitted fluorescence in larger volumes have to be made. Taking the spectral data shown in figure 2 into account and the UV wavelength of the collimated LED sources presently used (wavelength maximum 384 nm), we consider phantom volumes on the order of a litre to be do-able. This could be extended by using a long-wavelength, double-photon method of photo-excitation.

5. References

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