Electron Irradiation Effects of Radiochromic PCDA Vesicle Gel Dosimeters: Postprint

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Abstract

Gel dosimeters possess the unique capability to record three-dimensional (3D) radiation dose distributions, offering distinct advantages for dosimetry measurements in regions with steep dose gradients. In this study, a novel radiochromic gel dosimeter was developed by dispersing nanovesicles self-assembled from 10,12-pentacosadiynoic acid (PCDA) within a tissue-equivalent gel matrix. The characteristics of the radiochromic PCDA vesicle gel dosimeters were evaluated. Results indicate that these dosimeters exhibit a good linear response to 1.7 MeV electron beam irradiation across the dose range of 0.32–6.36 kGy. Furthermore, the radiochromic gel dosimeters overcome several limitations of existing gel dosimeters, including diffusion effects, post-irradiation effects, and poor formability. Consequently, the developed radiochromic PCDA vesicle gel dosimeters can be broadly applied to three-dimensional dose distribution measurements using optical readout techniques.

Full Text

Preamble

Electron Irradiation Effects of Radiochromic PCDA Vesicle Gel Dosimeters

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Gel dosimeters possess the unique capacity to record radiation dose distribution in three dimensions (3D), offering specific advantages for dosimetry measurements in regions with steep dose gradients. In this study, a novel radiochromic gel dosimeter was developed by dispersing nanovesicles self-assembled from 10,12-pentacosadiynoic acid (PCDA) into a tissue-equivalent gel matrix. The characteristics of these radiochromic PCDA vesicle gel dosimeters were systematically evaluated. Results indicate that the dosimeters exhibit a good linear response to 1.7 MeV electron beam irradiation in the dose range of 0.32–6.36 kGy. Furthermore, these radiochromic gel dosimeters overcome limitations of existing gel dosimeters such as diffusion effects, post-radiation effects, and poor formability. Consequently, the radiochromic PCDA vesicle gel dosimeters developed in this work could be broadly applied to 3D dose distribution measurement with optical readout.

Keywords: Radiochromic gel dosimeter, PCDA nanovesicle, 3D dose distribution measurement, Post-radiation effect
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Introduction

In radiotherapy and radiation processing applications, measuring three-dimensional (3D) dose distribution within a defined volume is often necessary. Conventional dosimetry systems—including calorimeters, ionization chambers, liquid chemical dosimeters (e.g., Fricke dosimeter), thermoluminescence dosimeters, and radiochromic film [1–4]—provide only point or two-dimensional dose information. In contrast, gel dosimeters, which contain uniformly distributed radiation-sensitive chemicals, are capable of recording radiation dose distribution in three dimensions [5, 6]. Upon irradiation, the chemical yield of products becomes a function of the absorbed radiation dose [7, 8]. Due to their high spatial resolution and dosimetric accuracy, gel dosimeters offer specific advantages for measurements in regions with steep dose gradients [5].

However, several types of gel dosimeters suffer from performance limitations. Fricke gel dosimeters fail to maintain spatial stability within a few hours after irradiation due to rapid diffusion of Fe^{2+} and Fe^{3+} ions [6, 9, 13]. Polymer gel dosimeters are plagued by reading deviations caused by oxygen contamination [5, 10, 14]—where oxygen quenches free radicals generated during irradiation and inhibits polymerization reactions—and by post-radiation effects [5], where monomers continue to polymerize after irradiation. Micelle gel dosimeters (e.g., leuco dye micelle gel dosimeters) are temperature-sensitive during irradiation

and tend to fade over time [11, 12]. They also exhibit relatively low dose sensitivity and may show significant dose-rate dependence [15]. Additionally, due to their poor formability, these gel dosimeters must be contained within vessels to maintain their shape, which reduces tissue equivalence.

The diacetylene 10,12-pentacosadiynoic acid (PCDA) serves as the reporter molecule in commercial Gafchromic film used for 2D dosimetry [16–18]. With a hydrophilic carboxyl head group and a hydrophobic tail, PCDA molecules can self-assemble into vesicles in aqueous solution [19, 20]. PCDA monomers can polymerize upon radiation exposure to generate blue-phase PDA vesicles without any precipitation. In this study, we developed a novel radiochromic gel dosimeter for 3D dose distribution measurement by dispersing PCDA self-assembled nanovesicles into a tissue-equivalent gel matrix. This nanovesicle design significantly overcomes dose image blurring caused by monomer diffusion while limiting polymer chain growth within vesicles, thereby reducing post-irradiation effects. The gel matrices exhibit excellent tissue equivalence and elastic properties, eliminating the need for container walls and avoiding optical problems associated with refractive index mismatches. They can be molded into desired shapes, providing a robust spatial structure for 3D dose distribution measurement. Thus, the radiochromic PCDA vesicle gel dosimeters offer superior performance compared to existing gel dosimeters and are generally suitable for 3D dose distribution measurement with optical readout.

Materials and Methods

A. PCDA Vesicles and Gel Preparation

The radiochromic gel consists of two components: the radiochromic system (PCDA vesicles) and the gel matrix system comprising organic matter and approximately 85% water (providing good radiation tissue equivalence). The fabrication process for the radiochromic PCDA vesicle gel dosimeter is illustrated schematically in Fig. 1 [Figure 1: see original paper].

Fig. 1. (Color online) Schematic illustration of the fabrication and application of radiochromic PCDA vesicle gel dosimeter.

The 10,12-pentacosadiynoic acid (PCDA, 98+% purity, Alfa Aesar Chemical Co. Ltd., China) served as the reporter molecule in the radiochromic gel. It was dissolved in acetone (CH_3COCH_3), and PCDA vesicles were prepared using the injection method. Monomers acrylamide (AA) and crosslinking agent N,N -methylene-bis-acrylamide (BIS) were dissolved in the PCDA vesicle solution. These components were polymerized and crosslinked under catalysis by ammonium persulfate ($(NH_4)_2S_2O_8$) to form the radiochromic gel. The acetone, AA, BIS, and $(NH_4)_2S_2O_8$ were all analytically pure and purchased from Chengdu Kelon Chemical Reagent Factory, China. Deionized water was used in all experiments.

B. PCDA Nanovesicles Preparation

PCDA nanovesicles were prepared using the injection method. PCDA crystalline powder was dissolved in acetone at a concentration of 20 mmol/L. This solution was injected into a defined volume of deionized water at temperatures above acetone' s boiling point (56 °C). The solution was maintained in a warm water bath and subjected to ultrasonic vibration for 10 minutes. After cooling to room temperature, the solution was placed in a 4 °C refrigerator for over six hours to obtain the PCDA vesicle solution, with a final PCDA concentration of 1 mmol/L. To observe the morphology, the vesicle solution was air-dried on silicon slices and copper grids, then characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

C. Radiochromic Gel Preparation

AA and BIS were added to the vesicle solution prepared in Sec. II B 1 and dissolved by ultrasound at concentrations of 2×10^3 mmol/L and 65 mmol/L, respectively. The solution was heated to 50–60 °C in a water bath, after which ammonium persulfate (catalyst) was added and stirred to maintain uniformity. The final ammonium persulfate concentration in the solution was 6 mmol/L. The solution temperature was maintained until the AA monomer was completely polymerized, forming a transparent gel.

D. Irradiation and Testing

Samples were irradiated with electron beams of 1 or 1.7 MeV from a JJ-2 model Van de Graaff accelerator at ambient temperature (25 °C) and 60% relative humidity.

1. Color Change Response to Irradiation Linearity of irradiation response represents a key technical indicator for gel dosimeters and must be calibrated before dose measurement. Gels prepared in a single batch were irradiated with 1.7 MeV electron beams for durations of 6.25, 12.50, 25.00, 37.50, 50.00, 62.50, 75.00, 93.75, and 125.00 s at a fluence rate of 10^{11} cm^{-2} s^{-1}. Electron fluences were converted to absorbed doses in the gels using Monte Carlo (M-C) methods. Absorption spectra of the gels were measured with a spectrophotometer (Shimadzu Corp., Japan) two hours after irradiation. Net optical density (net OD) is defined as the difference in optical density between irradiated and non-irradiated gel samples. The net OD-dose curve was plotted, and the fitting function and root mean square error were calculated.

2. Post-Radiation Effect Optical densities at the 680 nm absorption peak were measured at 0.1, 0.5, 1, 1.5, 2, 12, 24, 48, 72, and 168 h after 1.7 MeV electron beam irradiation at a fluence of 5×10^{12} cm^{-2} and fluence rate of 10^{11} cm^{-2} s^{-1}.

3. Diffusion Effect PCDA nanovesicles self-assembled from PCDA monomers can prevent diffusion of monomer molecules. To test the diffusion effect in the radiochromic gel, a gel slice (\$ $4.5cm)wasirradiatedwith1.7MeVelectronbeams($ \$2 cm beam spot) along the axial direction at a fluence of 5×10^{12} cm^{-2} and fluence rate of 10^{11} cm^{-2} s^{-1}. Photographs were taken in a dark room at 0.5 h and 96 h after irradiation, with gel samples placed on a white planar backlight source and a digital camera (Nikon D90, Japan) fixed directly above the gel. A bandpass filter ((680 $\pm$ 20) nm) was attached to the camera lens via a connecting tube, with a distance of 32 cm between the gel surface and camera lens. Camera parameters were: shutter speed 1/2 s, focal length 105 mm, aperture 5.6, ISO 1000, and resolution 4288 $\times$ 2848 pixels. Filtered photos were converted to gray-level images using Image-Pro Plus software. Gray levels were converted to net OD using Eq. (1):

$$\Delta OD = OD_{irr} - OD_{blank} = \lg(GL_{light}/GL_{irr}) - \lg(GL_{light}/GL_{blank}) = \lg(GL_{blank}/GL_{irr})$$

where OD represents optical density at 660–700 nm, ΔOD is net mean optical density, and GL denotes gray level. The radial net OD distributions derived from the two gel slice images (0.5 and 96 h) were compared.

4. Depth OD Distribution Test Two cylindrical gels (\$ \$4.5 cm $\times$ 2 cm) were prepared and irradiated with \$ \$2 cm electron beams of 1 and 1.7 MeV, respectively, along the axial direction at a fluence of 5×10^{12} cm^{-2} and fluence rate of 10^{11} cm^{-2} s^{-1}. The gels were then cut into slices (\$ \$4.5 cm $\times$ 0.3 cm), which were positioned with a 0.15 cm gap for photography using the same digital camera settings as in Sec. II B 3. The filtered photo (Fig. 9(c)) was converted to a gray-level image using Image-Pro Plus software, and gray levels along the line in the image were obtained. These gray levels were converted to net OD using Eq. (1). The depth-net OD distribution curve derived from the gel gray-level image was plotted.

Results and Discussion

A. Morphology of PCDA Nanovesicles

SEM and TEM images of the PCDA vesicles prepared in Sec. II B 1 are shown in Fig. 2 [Figure 2: see original paper]. The vesicles exhibit globular or ellipsoidal shapes with diameters of approximately 60 nm and display an obvious hollow structure. These results demonstrate that PCDA monomers in aqueous solution can self-assemble into hollow vesicles using the injection method, which offers simpler operation and higher yield compared to other vesicle preparation methods such as the membrane method and reverse evaporation. This approach is suitable for batch preparation of PCDA vesicle gel dosimeters.

Fig. 2. SEM (a) and TEM (b) images of PCDA nanovesicles.

The PCDA nanovesicles were evenly distributed within the radiochromic gel matrix. Upon irradiation, PCDA monomer molecules in the vesicles reacted to form blue-phase polydiacetylene (PDA) with conjugated double and triple bonds [19], as illustrated schematically in Fig. 3 [Figure 3: see original paper]. After gel irradiation with electron beams at fluences of 0.625×10^{12}–12.500×10^{12} cm^{-2} (0.32–6.36 kGy, as calculated by M-C methods), the polymerization reaction yield of monomers was approximately proportional to the absorbed dose. Figure 4 [Figure 4: see original paper] shows that gel samples gradually changed from colorless to dark blue as the absorbed dose increased.

Fig. 3. (Color online) Reaction schematics of PCDA before and after irradiation. (a) PCDA monomer reacting to form PDA polymer and (b) PCDA vesicle reacting to generate blue-phase PDA vesicle.

B. Response of PCDA Vesicle Gel Samples to Different Electron Doses

Figure 5 Figure 5: see original paper shows the absorption spectra of gel samples irradiated to different doses. The main absorption peak is located at 680 nm, with a minor peak near 625 nm. The amplitude of these absorption peaks increases with dose. Figure 5(b) displays net OD of the main absorption peak as a function of dose, revealing a good linear response in the dose range of 0.32–6.36 kGy with $R^2 = 0.9992$. The linear range of the dose response extends to 6.36 kGy.

Fig. 4. (Color online) Photos of gels irradiated by 1.7 MeV electrons at different doses.

Fig. 5. (Color online) Absorption spectra of PCDA vesicle gel samples measured two hours after irradiation to different doses (a), and net OD of the main absorption peak (680 nm) as a function of irradiation dose (b).

C. Post-Radiation Effect

The net OD of PCDA vesicle gel samples measured at various times after irradiation is shown in Fig. 6 [Figure 6: see original paper]. A 1.76% increase was observed at 2 h, with a further increase of 1.09% at 48 h, but no additional increase from 48 to 168 h. Therefore, the post-radiation effect proceeded rapidly within the first 2 hours after irradiation, continued at a slower pace up to 48 hours, and then ceased. Reading the optical density 2 h after irradiation can effectively improve dosimetric accuracy of the PCDA vesicle gel dosimeters. In contrast, other polymer gel dosimeters suffer from serious post-radiation effects due to free radical polymerization, undergoing rapid polymerization reactions during the first few hours after irradiation. For practical dosimetry, users are recommended to wait 10 hours before reading irradiated PAG gel and 30 hours for MAGIC gel [14]. The time required for a stable response in PCDA vesicle gel is substantially shorter than for these polymer gels. The reduced post-radiation effect may be attributed to limited polymer chain growth within the vesicles.

Fig. 6. Post-radiation effect of PCDA vesicle gel: net OD at 680 nm measured at different times after irradiation.

D. Diffusion Effect

Figure 7 [Figure 7: see original paper] shows gel slices before and after 2.54 kGy irradiation with $ 2cmelectronbeams.Theirradiatedareaturnedblue, insharpcontrasttothenon−irradiatedsurroundingregion.Filteredphotosofthegelslicewereretakenat0.5and96hafterirradiation(Figs.8(a)a levelimagesusingImage−ProPlussoftware.Graylevelsalonglinesintheimageswereobtainedandconvertedton seeoriginalpaper](c)showstheradialnetODdistributionsderivedfromthetwogelsliceimages(0.5and96h).Dueto radiationeffect, the96hsampleexhibitsslightlyhighernetODintheirradiatedareacomparedtothe0.5hsample.E heightwidthoftheODdistributioncurveremainsunchanged(±$9.9 mm), indicating that assembling PCDA monomers into nanovesicles effectively prevents diffusion of monomer molecules. No diffusion effects were observed in high dose gradient regions of PCDA vesicle gel samples, and the dose distribution image remains sharp.

Fig. 7. (Color online) Gel slices before (a) and after (b) irradiation by $ $2 cm electron beams.

Fig. 8. (Color online) Filtered (680 nm) photos of gel slices taken at 0.5 h (a) and 96 h (b) after irradiation, and their radial net OD distribution (c).

E. Depth OD Distribution Test

Two cylindrical gels irradiated by 1.0 and 1.7 MeV electron beams are shown in Fig. 9(a) [Figure 9: see original paper]. The maximum absorbed doses in the gels, calculated using Monte Carlo methods, were 2.80 kGy (at 1.7 mm depth) and 2.54 kGy (at 3.3 mm depth), respectively. Gel slices penetrated by the electron beams (Fig. 9(b)) were photographed with the same digital camera settings as in Sec. II B 3. The filtered photo (Fig. 9(c)) was converted to a gray-level image using Image-Pro Plus software, and gray levels along the line in Fig. 9(c) were obtained. These gray levels were converted to net optical densities using Eq. (1). The depth profiling of net OD derived from the gel gray-level image is shown in Fig. 10 [Figure 10: see original paper]. The energy deposition of electron beams in the gel is similar to that in human soft tissue: when electron beams enter the gel sample, energy deposition increases to a maximum value near the secondary electrons' maximum range, then decreases gradually.

Fig. 9. (Color online) Cylindrical gels irradiated by $ $2 cm electron beams (a), and normal (b) and filtered (c) photos of the irradiated gel slices.

Fig. 10. (Color online) Depth-net OD distribution curves of gels.

Conclusion

Due to their high spatial resolution, dose accuracy, and tissue equivalence, gel dosimeters have potential applications in 3D dose distribution measurement of

high dose gradient radiation fields. The radiation polymerization process of PCDA monomers is not affected by oxygen, and the polymerization product exhibits intense color, producing a response approximately proportional to absorbed dose [17].

In this study, nanovesicles self-assembled from PCDA monomers with amphiphilic surfactant structure were dispersed into a tissue-equivalent gel matrix to develop a novel radiochromic gel dosimeter. The nanovesicle design significantly overcomes dose image blurring caused by monomer molecule diffusion while limiting polymer chain growth within vesicles, thereby reducing post-radiation effects. The gel matrices prepared in this study possess excellent tissue equivalence and elastic strength and can be arbitrarily shaped or cut. Consequently, the radiochromic PCDA vesicle gel dosimeters developed in this work overcome limitations of existing gel dosimeters and are generally suitable for 3D dose distribution measurement with optical readout.

In this work, all optical density data were acquired from gel slices using a spectrophotometer or digital camera. However, the mechanical slicing technique is time-consuming and may reduce precision. In future work, if non-destructive scanning techniques can be successfully applied to radiochromic gel dosimeters, the overall efficiency and precision of the dosimetry system will be effectively enhanced.

References

[1] Poppe B, Blechschmidt A, Djouguela A, et al. Two-dimensional verification of IMRT plans using ionization chamber arrays. *Med Phys*, 2006, 33: 1005–1015. DOI: 10.1118/1.2179167

[2] Fricke H and Hart E J. Chemical dosimetry. *Radiation dosimetry*, 1966, 2: 167–239.

[3] Nakajima T, Murayama Y, Matsuzawa T, et al. Development of a new highly sensitive LiF thermoluminescence dosimeter and its applications. *Nucl Instrum Meth*, 1978, 157: 155–162. DOI: 10.1016/0029-554X(78)90601-8

[4] McLaughlin W L, Yun-Dong C, Soares C G, et al. Sensitometry of the response of a new radiochromic film dosimeter to gamma radiation and electron beams. *Nucl Instrum Meth*, 1991, 302: 165–176. DOI: 10.1016/0168-9002(91)90506-L

[5] Baldock C, De Deene Y, Doran S, et al. Polymer gel dosimetry. *Phys Med Biol*, 2010, 55: R1–R63. DOI: 10.1088/0031-9155/55/5/R01

[6] Schreiner L J. Review of Fricke gel dosimeters. *J Phys Conf Ser*, 2004, 3: 9–21. DOI: 10.1088/1742-6596/3/1/003

[7] Trapp J V, Bäck S Å J, Lepage M, et al. An experimental study of the dose response of polymer gel dosimeters imaged with x-ray computed tomography. *Phys Med Biol*, 2001, 46: 2939–2951. DOI: 10.1088/0031-9155/46/11/312

[8] MacDougall N D, Pitchford W G and Smith M A. A systematic review of the precision and accuracy of dose measurements in photon radiotherapy using polymer and Fricke MRI gel dosimetry. *Phys Med Biol*, 2002, 47: R107–R121. DOI: 10.1088/0031-9155/47/20/201

[9] Kelly R G, Jordan K J and Battista J J. Optical CT reconstruction of 3D dose distributions using the ferrous-benzoic-xylenol (FBX) gel dosimeter. *Med Phys*, 1998, 25: 1741–1750. DOI: 10.1118/1.598356

[10] De Deene Y, Vandecasteele J and Vercauteren T. Low-density polymer gel dosimeters for 3D radiation dosimetry in the thoracic region: A preliminary study. *J Phys Conf Ser*, 2013, 444: 12026–12029. DOI: 10.1088/1742-6596/444/1/012026

[11] Jordan K and Avvakumov N. Radiochromic leuco dye micelle hydrogels: I. Initial investigation. *Phys Med Biol*, 2009, 54: 6773–6789. DOI: 10.1088/0031-9155/54/22/002

[12] Babic S, Battista J and Jordan K. Radiochromic leuco dye micelle hydrogels: II. Low diffusion rate leuco crystal violet gel. *Phys Med Biol*, 2009, 54: 6791–6808. DOI: 10.1088/0031-9155/54/22/003

[13] Harris P J, Piercy A and Baldock C. A method for determining the diffusion coefficient in Fe (II/III) radiation dosimetry gels using finite elements. *Phys Med Biol*, 1996, 41: 1745–1753. DOI: 10.1088/0031-9155/41/9/013

[14] De Deene Y, Venning A, Hurley C, et al. Dose-response stability and integrity of the dose distribution of various polymer gel dosimeters. *Phys Med Biol*, 2002, 47: 2459–2470. DOI: 10.1088/0031-9155/47/14/307

[15] Vandecasteele J, Ghysel S, Baete S H, et al. Radio-physical properties of micelle leucodye 3D integrating gel dosimeters. *Phys Med Biol*, 2011, 56: 627–651. DOI: 10.1088/0031-9155/56/3/007

[16] Niroomand-Rad A, Blackwell C R, Coursey B M, et al. Radiochromic film dosimetry: recommendations of AAPM radiation therapy committee task group 55. *Med Phys*, 1998, 25: 2093–2115. DOI: 10.1118/1.598407

[17] Rink A, Lewis D F, Varma S, et al. Temperature and hydration effects on absorbance spectra and radiation sensitivity of a radiochromic medium. *Med Phys*, 2008, 35: 4545–4555. DOI: 10.1118/1.2975483

[18] Sun P, Jiang B, He J, et al. Gamma ray radiation study on sensitive radiochromic films. *Nucl Tech*, 2009, 32: 273–276. (in Chinese) DOI: 10.3321/j.issn:0253-3219.2009.04.008

[19] Okada S, Peng S, Spevak W, et al. Color and chromism of polydiacetylene vesicles. *Acc Chem Res*, 1998, 31: 229–239. DOI: 10.1021/ar970063v

[20] Pires A C S, Soares N F F, da Silva L H M, et al. A colorimetric biosensor for the detection of foodborne bacteria. *Sensor Actuat B-Chem*, 2011, 153: 17–23. DOI: 10.1016/j.snb.2010.09.069