



UNIVERSITI PUTRA MALAYSIA

**DEVELOPMENT OF NORMOXIC POLYMER GEL DOSIMETERS BASED
ON HYDROXYETHYLACRYLATE AND
HYDROXYETHYLMETHACRYLATE MONOMERS AND THEIR
CHARACTERIZATIONS USING RAMAN SPECTROSCOPY AND
MAGNETIC RESONANCE IMAGING SCANNER**

AZHAR ABDUL RAHMAN

FS 2009 21



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By

AZHAR ABDUL RAHMAN

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

April 2009



In the Name of Allâh, the Most Gracious, the Most Merciful

This work is dedicated to my beloved wife, Arnie Fadzilah and my beloved daughters, Nur Afiqah, Nur Athirah, Nur Aqilah and also to the memory of my dad Abdul Rahman Omar.



Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of requirement for the degree of Doctor of Philosophy

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AZHAR ABDUL RAHMAN

April 2009

Chairman : Professor Elias Saion, PhD

Faculty : Science

Polymer gel dosimeters in conjunction with the nuclear magnetic resonance imaging (MRI) are potentially useful for verification of complex dose distributions in three dimensions (3D) applied in radiotherapy treatment planning. The radiation-induced normoxic polymer gels of polyhydroxyethylacrylate (PHEAG) and polyhydroxyethylmethacrylate (PHEMAG) have been studied using Raman spectroscopy and MRI scanner. The studies are focused on PHEAG and PHEMAG because these monomers belong to acrylic group. Most of the monomer in the acrylic group will indicate physical changes dramatically due to radiation given. The PHEAG



and PHEMAG were synthesized from 2-hydroxyethylacrylate (HEA) and hydroxyethylmethacrylate (HEMA) monomer (2 to 5% w/w) respectively and together with methylene-bis-acrylamide (BIS) crosslinker (1 to 4% w/w), gelatine (3% w/w), ascorbic acid (5 mM to 15 mM) and completed with de-ionized water. The dosimeters were irradiated with ^{60}Co teletherapy γ -rays source at a constant dose rate of 0.177 Gy/min, receiving doses up 20 Gy for the single point dose measurement and the 3D dose distributions scanning.

The polymerization intended for PHEMAG was followed by the change of Raman intensity at Raman shift of 812 cm^{-1} , 1978 cm^{-1} and 2885 cm^{-1} assigned for C-C stretching, C=O stretching and CH_3 stretching respectively and at 812 cm^{-1} assigned for C-C stretching in favour of PHEAG. The Raman intensity y corresponding to the amount of polymer formed in both PHEAG and PHEMAG increases with increasing dose D and follows a mono-exponential equation given as $y = y_0 + A(1 - e^{-D/D_0})$. The dose sensitivity D_0 derived from the equation and k factor derived from a linear relationship between D_0 and co-monomer concentration were found increasing with the increase of initial concentrations of monomer, cross-linker and anti-oxidant. The consumptions of co-monomers in PHEAG were studied by a decrease intensity of C=C stretching at 2887 cm^{-1} and 2602 cm^{-1} of HEA and BIS respectively and at 2602 cm^{-1} and 2369 cm^{-1} of HEMA and BIS respectively in favour of PHEMAG. The intensity decreases with increasing dose and follows mono-exponential equation given as $y = y_0 - A(1 - e^{-D/D_0})$. The dose sensitivity D_0 and k factor were also found



to increase with the increase of monomer, cross-linker and anti-oxidant concentrations.

The PHEMAG phantoms synthesized from HEMA monomer (3% w/w), BIS crosslinker (2 to 4% w/w), gelatine (3%), anti-oxygen ascorbic acid (15 mM to 55 mM) and completed with de-ionized water were exposed with single and crossed beams to simulate radiotherapy treatment. Magnetic resonance imaging (MRI) scanner was used to scan dose distribution of the phantoms and the 3D images were evaluated using a digital densitometer. It was found that the absorbed dose decreases with the increase of depth dose inside the phantom and the consequently two crossed beams of 20 Gy each produced less than 35 Gy beyond 3 cm depth dose. There is a slightly increase in dose with the increase of ascorbic acid concentration for all the radiation beams tested, indicating the use of ascorbic acid alone as anti-oxidant agent in PHEMAG was able to produce normoxic polymer gel dosimeters. Referring to the results of dose correlation factor k , it can be concluded that k_{HEMA} is more significant than k_{HEA} .

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan untuk ijazah Doktor Falsafah

**PEMBANGUNAN METER DOS POLIMER GEL “NORMOXIC”
BERASASKAN MONOMER HIDROKSJETILAKRILAT DAN
HIDROKSJETILMETAKRILAT DAN PENCIRIANNYA MENGGUNAKAN
SPEKTROSKOPI RAMAN DAN PENGIMBAS PENGIMEJAN AYUNAN
MAGNET**

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Perhubungan antara dosimeter polimer gel dengan MRI berpotensi digunakan untuk verifikasi penyerakan dos kompleks dalam bentuk tiga dimensi untuk rawatan radioterapi. Radiasi aruhan polimer gel “normoxic” polihidroksietilakrilat (PHEAG) dan polihidroksietilmetakrilat (PHEMAG) telah dikaji dengan menggunakan spektroskopi Raman and pengimbas MRI. Kajian tertumpu terhadap PHEAG dan PHEMAG kerana monomer-monomer ini berada di dalam kumpulan akrilik. Kebanyakan monomer daripada kumpulan akrilik akan menunjukkan perubahan fizikal yang ketara akibat sinaran yang diberikan. PHEAG and PHEMAG telah



disintesis dari 2-hidroksietilakrilat (HEA) dan 2-hidroksietilmetakrilat (HEMA) (2 hingga 5% w/w) masing-masing dan bersama-sama dengan methylene-bis-acrylamide (BIS) taut-silang (1 hingga 4% w/w), gelatin (3%), asid askorbik (5 mM hingga 15 mM) dan disudahi dengan air ternyah ion. Dosimeter tersebut telah diradiasikan dengan sumber teleterapi sinar- γ ^{60}Co pada kadar tetap 0.177 Gy/min, menerima dos sehingga 20 Gy untuk pengukuran dos titik tunggal dan pengimbasan taburan dos 3D.

Pempolimeran PHEMAG yang disasarkan telah diikuti dengan perubahan regangan anjakan keamatan Raman pada 812 cm^{-1} , 1978 cm^{-1} dan 2885 cm^{-1} diwakili untuk regangan C-C, regangan C=O dan juga regangan CH_3 masing-masing dan pada 812 cm^{-1} diwakili untuk regangan C-C terhadap PHEAG. Keamatan Raman y mempunyai kesamaan bilangan polimer yang terbentuk di dalam kedua-dua PHEAG dan PHEMAG meningkat dengan peningkatan dos D dan mengikut persamaan mono-eksponen yang dinyatakan sebagai $y = y_0 + A(1 - e^{-D/D_0})$. Kepekaan dos D_0 yang diperolehi daripada persamaan dan faktor k yang diperolehi daripada hubungan linear antara D_0 dan kepekatan monomer bersama telah didapati meningkat dengan peningkatan kepekatan pemulaan monomer, taut-silang dan anti-oksida. Penggunaan monomer di dalam PHEAG telah dikaji dengan pengurangan keamatan regangan C=C pada 2887 cm^{-1} dan 2602 cm^{-1} daripada HEA dan BIS masing-masing dan pada 2602 cm^{-1} dan 2369 cm^{-1} daripada HEMA dan BIS masing-masing terhadap PHEMAG. Keamatan berkurangan dengan peningkatan dos dan mematuhi persamaan mono-eksponen yang diberi sebagai $y = y_0 - A(1 - e^{-D/D_0})$. Kepekaan dos D_0 dan



faktor k juga didapati meningkat dengan peningkatan monomer, tautan-silang dan kepekatan anti-oksida.

Fentom PHEMAG yang telah disintesis daripada monomer HEMA (3% w/w), BIS (2 hingga 4% w/w), gelatin (3%), anti-oksida asid askorbik (15 mM hingga 55 mM) dan disudahi dengan air ternyah ion telah didedahkan dengan pancaran tunggal dan silang untuk merangsang rawatan radiotherapi. Pengimbas Pengimejan Resonan Magnet (MRI) telah digunakan untuk mengimbas taburan dos oleh fentom dan imej 3D telah dinilai dengan densitometer digital. Didapati penyerapan dos berkurangan dengan peningkatan kedalaman dos di dalam fentom dan menyebabkan dua pancaran silang 20 Gy setiap satu menghasilkan kurang daripada 35 Gy melangkaui 3 cm kedalaman dos. Terdapat sedikit peningkatan di dalam dos dengan peningkatan kepekatan asid askorbik untuk semua pancaran radiasi yang telah diuji, menunjukkan penggunaan asid askorbik sendirian sebagai agen anti-oksida di dalam PHEMAG boleh menghasilkan meter dos polimer gel “normoxic”. Berdasarkan kepada keputusan yang diperolehi untuk faktor dos korelasi k , dapt dirumuskan bahawa k_{HEMA} adalah lebih menonjol daripada k_{HEA} .

ACKNOWLEDGEMENTS

All the praise and admiration for Allah, the Almighty, Beneficial and the most Merciful, who has enabled me to submit this thesis.

My thanks and upmost appreciation goes to my thesis committee members, Prof. Dr. Elias Saion, Chairman of the Supervisory Committee who has been very helpful in providing me intellectual guidance, as well as to Prof. Dr. Kaida Khalid, Assoc. Prof Dr. Mohamad Zaki A. Rahman and Dr. Noriah Mod Ali who is sincerely help me throughout my studies. This work would not have been possible without the support and encouragement from them. I would like to express my kind appreciation to my friends and lab-mates Mr. Mohd. Zain, Mr. Iskandar Shahrim, Dr. Khalid Ahmed Majali Raba'eh, and Dr. Mohammad Ahmad for their assistance and help during the research.

Thanks also to Secondary Standard Dosimetry Laboratory (SSDL), Malaysian Nuclear Agency and Department of Biomedical Imaging, Universiti Malaya Medical Centre (UMMC) for their cooperation and consent for me to use their equipment in completing my research. I would also like to thank Universiti Sains Malaysia (USM) and Ministry of Higher Education for the award of the Academic Staff Training Scheme (ASTS) Fellowship, which has supported me during my three years of research.

Last but not least it would not be complete for me without thanking my mother, Puan Azizah Hj. Chik for my upbringing and for the support of my receiving high education. I am thankful also to my wife and my daughters on whose constant encouragement and love I have relied throughout my time at Universiti Putra Malaysia (UPM). It is to them that I dedicate this work.



I certified that an Examination Committee met on 31 March 2009 to conduct the final examination of Azhar Bin Abdul Rahman on his Doctor of Philosophy thesis entitled “Development and Raman Spectroscopy and Magnetic Resonance Imaging Characterization of Normoxic Polymer Gel Dosimeters Based on Hydroxyethylacrylate and Hydroxyethylmethacrylate Monomers” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

AZHAR ABDUL RAHMAN

Date: May 2009



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Figure 5.11	Dose correlation factor k_{BIS} of C-C stretching at 812 cm^{-1} of PHEAG due to BIS crosslinking at (a) 5 mM, (b) 10 mM and (c) 15 mM ascorbic acid.	5.20
Figure 5.12	Normalised Raman intensity of C-C stretching (812 cm^{-1}) showing the formation of PHEAG at (a) 2% HEA 1% BIS, (b) 3% HEA 1% BIS, (c) 4% HEA 1% BIS and (d) 5% HEA 1% BIS for different ascorbic acid concentration.	5.22
Figure 5.13	Normalised Raman intensity of C-C stretching (812 cm^{-1}) showing the formation of PHEAG at (a) 2% HEA 2% BIS, (b) 3% HEA 2% BIS, (c) 4% HEA 2% BIS and (d) 5% HEA 2% BIS for different ascorbic acid concentration.	5.23
Figure 5.14	Normalised Raman intensity of C-C stretching (812 cm^{-1}) showing the formation of PHEAG at (a) 2% HEA 3% BIS, (b) 3% HEA 3% BIS, (c) 4% HEA 3% BIS and (d) 5% HEA 3% BIS for different ascorbic acid concentration.	5.24
Figure 5.15	Normalised Raman intensity of C-C stretching (812 cm^{-1}) showing the formation of PHEAG at (a) 2% HEA 4% BIS, (b) 3% HEA 4% BIS, (c) 4% HEA 4% BIS and (d) 5% HEA 4% BIS for different ascorbic acid concentration.	5.25
Figure 5.16	Normalised Raman intensity of C=C stretching of HEA showing the consumption of HEA at (a) 1%, (b) 2%, (c) 3%, and (d) 4% BIS and for different HEA concentrations at 5 mM ascorbic acid.	5.27
Figure 5.17	Normalised Raman intensity of C=C stretching of HEA showing the consumption of HEA at (a) 1%, (b) 2%, (c) 3%, and (d) 4% BIS and for different HEA concentrations at 10 mM ascorbic acid.	5.28
Figure 5.18	Normalised Raman intensity of C=C stretching of HEA showing the consumption of HEA at (a) 1%, (b) 2%, (c) 3%, and (d) 4% BIS and for different HEA concentrations at 15 mM ascorbic acid.	5.29
Figure 5.19	Correlation between D_0 and the initial concentration of HEA for different BIS composition at (a) 5 mM, (b) 10 mM and (c) 15 mM ascorbic acid for the consumption of monomer at C=C stretching (2887 cm^{-1}).	5.31



Figure 5.20	Normalised Raman intensity of C=C stretching (2887 cm^{-1}) showing the formation of PHEAG at (a) 2% HEA 1% BIS, (b) 3% HEA 1% BIS, (c) 4% HEA 1% BIS and (d) 5% HEA 1% BIS for different ascorbic acid concentration.	5.33
Figure 5.21	Normalised Raman intensity of C=C stretching (2887 cm^{-1}) showing the formation of PHEAG at (a) 2% HEA 2% BIS, (b) 3% HEA 2% BIS, (c) 4% HEA 2% BIS and (d) 5% HEA 2% BIS for different ascorbic acid concentration.	5.34
Figure 5.22	Normalised Raman intensity of C=C stretching (2887 cm^{-1}) showing the formation of PHEAG at (a) 2% HEA 3% BIS, (b) 3% HEA 3% BIS, (c) 4% HEA 3% BIS and (d) 5% HEA 3% BIS for different ascorbic acid concentration.	5.35
Figure 5.23	Normalised Raman intensity of C=C stretching (2887 cm^{-1}) showing the formation of PHEAG at (a) 2% HEA 4% BIS, (b) 3% HEA 4% BIS, (c) 4% HEA 4% BIS and (d) 5% HEA 4% BIS for different ascorbic acid concentration.	5.36
Figure 5.24	Normalised Raman intensity of C=C stretching of BIS showing the consumption of BIS at (a) 2%, (b) 3%, (c) 4%, and (d) 5% HEA and for different BIS concentrations at 5 mM ascorbic acid.	5.38
Figure 5.25	Normalised Raman intensity of C=C stretching of BIS showing the consumption of BIS at (a) 2%, (b) 3%, (c) 4%, and (d) 5% HEA and for different BIS concentrations at 10 mM ascorbic acid.	5.39
Figure 5.26	Normalised Raman intensity of C=C stretching of BIS showing the consumption of BIS at (a) 2%, (b) 3%, (c) 4%, and (d) 5% HEA and for different BIS concentrations at 15 mM ascorbic acid.	5.40
Figure 5.27	Correlation between D_0 and the initial concentration of BIS for different HEA composition at (a) 5 mM, (b) 10 mM and 15 mM ascorbic acid for the consumption of crosslinker at C=C stretching (2377 cm^{-1}).	5.42
Figure 5.28	Normalised Raman intensity of C=C stretching (2377 cm^{-1}) showing the formation of PHEAG at (a) 1% BIS 2% HEA, (b) 2% BIS 2% HEA, (c) 3% BIS 2% HEA and (d) 4% BIS 2% HEA for different ascorbic acid concentration.	5.43



Figure 5.29	Normalised Raman intensity of C=C stretching (2377 cm^{-1}) showing the formation of PHEAG at (a) 1% BIS 3% HEA, (b) 2% BIS 3% HEA, (c) 3% BIS 3% HEA and (d) 4% BIS 3% HEA for different ascorbic acid concentration.	5.44
Figure 5.30	Normalised Raman intensity of C=C stretching (2377 cm^{-1}) showing the formation of PHEAG at (a) 1% BIS 4% HEA, (b) 2% BIS 4% HEA, (c) 3% BIS 4% HEA and (d) 4% BIS 4% HEA for different ascorbic acid concentration.	5.45
Figure 5.31	Normalised Raman intensity of C=C stretching (2377 cm^{-1}) showing the formation of PHEAG at (a) 1% BIS 5% HEA, (b) 2% BIS 5% HEA, (c) 3% BIS 5% HEA and (d) 4% BIS 5% HEA for different ascorbic acid concentration.	5.46
Figure 5.32	Normalised Raman intensity of C-C stretching showing the formation of PHEMAG at (a) 2%, (b) 3%, (c) 4%, and (d) 5% HEMA and for different BIS concentrations at 5 mM ascorbic acid.	5.48
Figure 5.33	Normalised Raman intensity of C-C stretching showing the formation of PHEMAG at (a) 2%, (b) 3%, (c) 4%, and (d) 5% HEMA and for different BIS concentrations at 10 mM ascorbic acid.	5.49
Figure 5.34	Normalised Raman intensity of C-C stretching showing the formation of PHEMAG at (a) 2%, (b) 3%, (c) 4%, and (d) 5% HEMA and for different BIS concentrations at 15 mM ascorbic acid.	5.50
Figure 5.35	Correlation between D_o and the initial concentration of HEMA for different BIS concentration at (a) 5 mM, (b) 10 mM and (c) 15 mM ascorbic acid for the formation of PHEMAG due to C-C stretching at 812 cm^{-1} .	5.52
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