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

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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

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

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April 2009

Chairman : Professor Elias Saion, PhD

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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-hdroxyethylacrylate (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 $y = y_0 + A\left(1 - e^{-D/D_0}\right)$. 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 $y = y_0 - A\left(1 - e^{-D/D_0}\right)$. 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 HIDROKSIETILAKRILAT DAN HIDROKSIETILMETAKRILAT 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. Kebanyakkan monomer daripada kumpulan akrilik akan menunjukkan perubahan fizikal yang ketara akibat sinaran yang diberikan. PHEAG and PHEMAG telah

disintesiskan daripada 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 $y = y_0 + A\left(1 - e^{-D/D_0}\right)$. Kepekaan dos D_o yang diperolehi daripada persamaan dan faktor k yang diperolehi daripada hubungan linear antara D_o 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 $y = y_0 - A\left(1 - e^{-D/D_0}\right)$. Kepekaan dos D_o 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}.

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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 of concurrently submitted for any other degree at UPM or other institutions.

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AZHAR ABDUL RAHMAN

Date: May 2009

LIST OF TABLES

Table		Page
Table 2.1	Different formulations published for normoxic polymer gels.	2.6
Table 2.2	Vibrational band assignments for acrylamide (AAm) BIS-acrylamide and polyacrylamide.	2.15
Table 2.3	R_2-dose sensitivity, $R_2(0)$ and correlation coefficient of PAGAT polymer gel between 0 Gy and 7 Gy (Venning et al., 2005).	2.33
Table 2.4	Gel compositions investigated by Karlsson et al. (2007).	2.36
Table 4.1	Various mixture of PHEMAG at 1% BIS and 5 mM ascorbic acid.	4.3
Table 4.2	Various mixture of PHEMAG at 2% BIS and 5 mM ascorbic acid.	4.4
Table 4.3	Various mixture of PHEMAG at 3% BIS and 5 mM ascorbic acid.	4.4
Table 4.4	Various mixture of PHEMAG at 4% BIS and 5 mM ascorbic acid.	4.4
Table 4.5	Various mixture of PHEMAG at 1% BIS and 10 mM ascorbic acid.	4.5
Table 4.6	Various mixture of PHEMAG at 2% BIS and 10 mM ascorbic acid.	4.5
Table 4.7	Various mixture of PHEMAG at 3% BIS and 10 mM ascorbic acid.	4.5
Table 4.8	Various mixture of PHEMAG at 4% BIS and 10 mM ascorbic acid.	4.6
Table 4.9	Various mixture of PHEMAG at 1% BIS and 15 mM ascorbic acid.	4.6
Table 4.10	Various mixture of PHEMAG at 2% BIS and 15 mM ascorbic acid.	4.6

Table 4.11	Various mixture of PHEMAG at 3% BIS and 15 mM ascorbic acid.	4.7
Table 4.12	Various mixture of PHEMAG at 4% BIS and 15 mM ascorbic acid.	4.7
Table 4.13	Various mixture of PHEAG at 1% BIS and 5 mM ascorbic acid.	4.8
Table 4.14	Various mixture of PHEAG at 2% BIS and 5 mM ascorbic acid.	4.9
Table 4.15	Various mixture of PHEAG at 3% BIS and 5 mM ascorbic acid.	4.9
Table 4.16	Various mixture of PHEAG at 4% BIS and 5 mM ascorbic acid.	4.9
Table 4.17	Various mixture of PHEAG at 1% BIS and 10 mM ascorbic acid.	4.10
Table 4.18	Various mixture of PHEAG at 2% BIS and 10 mM ascorbic acid.	4.10
Table 4.19	Various mixture of PHEAG at 3% BIS and 10 mM ascorbic acid.	4.10
Table 4.20	Various mixture of PHEAG at 4% BIS and 10 mM ascorbic acid.	4.11
Table 4.21	Various mixture of PHEAG at 1% BIS and 15 mM ascorbic acid.	4.11
Table 4.22	Various mixture of PHEAG at 2% BIS and 15 mM ascorbic acid.	4.11
Table 4.23	Various mixture of PHEAG at 3% BIS and 15 mM ascorbic acid.	4.12
Table 4.24	Various mixture of PHEAG at 4% BIS and 15 mM ascorbic acid.	4.12
Table 4.25	Various mixture of PHEMAG at 3% 2-hydroxyethyl methacrylate (HEMA), 2-4 %BIS and 15 mM ascorbic acid.	4.14

Table 4.26	Various mixture of PHEMAG at 3% 2-hydroxyethyl methacrylate (HEMA), 2-4 %BIS and 35 mM ascorbic acid.	4.14
Table 4.27	Various mixture of PHEMAG at 3% 2-hydroxyethyl methacrylate (HEMA), 2-4 %BIS and 55 mM ascorbic acid.	4.14
Table 4.28	Error analysis gained from densitometer measurements.	4.27
Table 5.1	Comparison between k_{HEA}, k_{HEMA} and k_{BIS} of PHEAG and PHEMAG.	5.112

LIST OF FIGURES

Figures		Page
Figure 2.1	Schematic representations of the different monomers used in the polymer gel dosimeter formulations.	2.4
Figure 2.2	Reaction scheme for the scavenging of oxygen by ascorbic acid.	2.10
Figure 2.3	Chemical structure of acrylamide, *N,N'*-methylene-bisacrylamide and Polyacrylamide gel (PAG).	2.13
Figure 2.4	Variation in FT-Raman spectra of polymerized PAG samples with absorbed radiation dose (Baldock et al., 1998b).	2.16
Figure 2.5	Variation of integrated peak areas of the acrylamide (1285 cm^{-1}) and bis-acrylamide (1256 cm^{-1}) vinyl δCH_2 vibrational bands with absorbed radiation dose (Baldock et al., 1998b).	2.17
Figure 2.6	Correlation of the vinyl CH_2 bending mode of bis (1256 cm^{-1}) and acrylamide (1285 cm^{-1}): (*a*) lines between points as a visual aid only; (*b*) data fitted to exponential (Jirasek et al., 2001).	2.18
Figure 2.7	Polymer formation observed in FT-Raman spectra of irradiated PAG. (*a*) 27 cm^{-1} mode, origin unknown, (*b*) 1126 cm^{-1} C–C stretch, (*c*) 1450 cm^{-1} CH_2 bend and (*d*) 2936 cm^{-1} CH_2 stretching mode of polyacrylamide (Jirasek et al., 2001)..	2.19
Figure 2.8	Integrated peak intensity of the 2936 cm^{-1} CH_2 stretch in polyacrylamide as a function of dose: (*a*) lines between points as a visual aid only, (*b*) data fitted to exponential. (Jirasek et al., 2001).	2.21
Figure 2.9	The half-dose, $D_{1/2}$, determined by FT-Raman spectroscopy for BIS and AA as a: (a) function of gelatine concentration and (b) function of the concentration of the monomers (Lepage et al., 2001c).	2.22
Figure 2.10	FT-Raman spectra for one of the HEA gels. Spectra corresponding to each absorbed dose were obtained (Gustavsson et al., 2004).	2.23

Figure 2.11	The consumption of BIS and HEA as a function of absorbed dose, measured using FT-Raman spectroscopy (Gustavsson et al., 2004).	2.24
Figure 2.12	Monoexponential function of Raman intensity Δy vs. dose D for polymerization process of polyacrylamide gel (PAAmG) for (a) 4% BIS at various AAm from 2 to 6% and for (b) 4% AAm at various BIS from 2 to 6% (Saion *et al.*, 2005a).	2.25
Figure 2.13	Monoexponential function of Raman intensity Δy vs. dose D (a) 4% BIS at various AAm from 2 to 6% for consumption of AAm and (b) 4% AAm at various BIS from 2 to 6% for consumption of BIS (Saion *et al.*, 2005a).	2.25
Figure 2.14	The polymerization process shows the correlation between (a) $D_{1/2}$ vs. % AAm at various BIS from 2 to 6% and (b) $D_{1/2}$ vs. % BIS at various AAm from 2 to 6% (Saion *et al.*, 2005a).	2.26
Figure 2.15	The co-monomer consumption process shows the correlation between (a) $D_{1/2}$ vs. % AAm at various BIS from 2 to 6% and (b) $D_{1/2}$ vs. % BIS at various AAm from 2 to 6% (Saion *et al.*, 2005a).	2.26
Figure 2.16	Spin–lattice relaxation rate plotted against absorbed dose for five different manufactured batches of gels of the same recipe (Baldock et al., 1998a).	2.28
Figure 2.17	Glass tubes containing VIPAR-gels. Gel A: non-irradiated. Gel B: absorbed 8 Gy integrated dose. The light part of gel C absorbed 11 Gy integrated dose while the transparent part did not absorb any dose (Pappas et al., 1999).	2.29
Figure 2.18	T_2 calculated map (axial section) of the phantom that contains test objects and the first batch of VIPAR gels. The dose that each gel has absorbed is presented in figure next to the T_2 calculated map. As the absorbed dose is increased the gels appear darker (T_2 is decreased) (Pappas et al., 1999).	2.30
Figure 2.19	Dose response of VIPAR gels. Measurements of both batches of gels are presented: ♦, first batch; O, second batch. A linear relationship between absorbed dose, D (Gy) and spin–spin relaxation rate, R_2 (s^{-1}) is observed. The full line represents the fit to both sets of data (Pappas et al.,	2.30

1999).

Figure 2.20 Spin-echo image of a 6% MAGIC plastic phantom irradiated with two square x-ray beams to 15 GY from the bottom and side of the image; TE = 300 ms, TR = 2000 ms (Fong et al., 2001). 2.31

Figure 2.21 R_2-dose response curve of the PAGAT polymer gel dosimeter evaluated at 12 h, 7 days and 24 days post-irradiation (Venning et al., 2005). 2.32

Figure 2.22 Dose resolution of the PAGAT polymer gel dosimeter evaluated at 12h, 7 days and 24 days post-irradiation (Venning et al., 2005). 2.33

Figure 2.23 Dose response curves obtained in a low-density normoxic polymer gel containing different concentrations of the antioxidant THP. The concentrations of THP were (a) 50 mM, (b) 75 mM and (c) 100 mM (Haraldsson et al., 2006). 2.34

Figure 2.24 Central gel depth dose curves (circles) compared with Monte Carlo calculations (full curve). The concentrations of THP were (a) 50 mM, (b) 75 mM and (c) 100 mM (Haraldsson et al., 2006). 2.35

Figure 2.25 The R_2 dose response for nMAG samples (2%MAA) irradiated to absorbed doses of up to 10 Gy (Karlsson et al., 2007). 2.37

Figure 2.26 R_2 versus the total absorbed dose for the nPAG (3%AA / 3%BIS) (Karlsson et al., 2007). 2.37

Figure 2.27 The slope of the dose response for the various fractionation schemes versus the dose per fraction for the nMAG dosimeter (2% MAA) (Karlsson et al., 2007). 2.38

Figure 2.28 R_2 dose response for nMAG 2% MAA, 4% MAA, 6% MAA, 8% MAA irradiated to absorbed doses of up to 10 Gy (Karlsson et al., 2007). 2.38

Figure 2.29 A gel irradiated with a highly-conformal dose distribution produced by a Gamma knife treatment unit. The distribution can be appreciated qualitatively without the need of imaging systems or processing (Ibbott et al., 1997). 2.41

Figure 2.30	The variation in LET as a function of depth for a monoenergetic proton beam (dashed curve, left-hand scale) and the measured relative sensitivity for the gel dosimeter (full curve, right-hand scale) (Gustavsson et al. 2004).	2.44
Figure 3.1	Schematic diagram of Compton Scattering.	3.6
Figure 3.2	Schematic diagram of pair production process for γ-radiation being interfered in the nucleus field and orbital electron to produce triplet particles.	3.9
Figure 3.3	Arrangement for Raman spectroscopy. Scattered radiation is monitored at perpendicular to the incident radiation.	3.16
Figure 3.4	Energy level diagram for Raman scattering; (a) stokes Raman scattering and (b) anti-Stokes Raman Scattering.	3.18
Figure 3.5	Transverse relaxation phenomena induce an increasing dephasing of individual spins in order to observe a progressive decrease of the macroscopic magnetization.	3.25
Figure 3.6	Schematic representation of a CPMG pulse sequence.	3.28
Figure 3.7	Schematic ball and stick representation of a polymer backbone in interaction with water molecules. It is noted that water protons can readily exchange with protons from NH groups but have a very slow exchange rate with protons on CH_2 groups.	3.30
Figure 3.8	Schematic representation of a magnetization transfer experiment.	3.32
Figure 3.9	Principle of spot light densitometry.	3.32
Figure 4.1	Polymer gel dosimeters containing 2-hydroxyethyl methacrylate (HEMA), *N*, *N*'-methylene-bisacrylamide (BIS), ascorbic acid, gelatine, and deionized water in 5 ml ampoule tubes sealed with parafilm tape.	4.3
Figure 4.2	Polymer gel dosimeters containing 2-hydroxyethyl acrylate (HEA), *N*, *N*'-methylene-bisacrylamide (BIS), ascorbic acid, gelatine, and deionized water in 5 ml ampoule tubes sealed with parafilm tape.	4.8

Figure 4.3	Polymer gel dosimeters containing 2-hydroxyethyl methacrylate (HEMA), *N, N'*-methylene-bisacrylamide (BIS), ascorbic acid, gelatine, and deionized water in (a) glass tubes and (b) petry dish sealed with parafilm tape.	4.13
Figure 4.4	^{60}Co gamma rays chamber of Eldorado 8, Secondary Standard Dosimetry Laboratory (SSDL), Malaysian Nuclear Agency, Bangi, Selangor.	4.15
Figure 4.5	Eldorado 8 control panel.	4.16
Figure 4.6	Perspex sample holder.	4.17
Figure 4.7	Sample holder positioned 5 cm from Field Surface (FS) in water phantom.	4.18
Figure 4.8	Polymer gel dosimeter for MRI scanning showing (a) un-irradiated and (b) irradiated.	4.19
Figure 4.9	Raman standard peaks for Isopropyl Alcohol.	4.21
Figure 4.10	Raman spectrometer (RSI 2001G, Raman System, Inc.) (a) equipped with 532 nm solid state diode and (b) complete system with computer aided data acquisition devices.	4.22
Figure 4.11	Whole-body Siemens Magnetom SP 1.5 T (Siemens, Germany) clinical MRI scanners, Department of Biomedical Imaging, University Malaya Medical Centre (UMMC), Kuala Lumpur.	4.24
Figure 4.12	A custom made polystyrene container to hold the samples.	4.24
Figure 4.13	Radiological film obtained from MRI slice scans.	4.25
Figure 4.14	Digital densitometer (Victoreen, model 07-440, USA), Biophysics Lab, Department of Physics, Universiti Putra Malaysia.	4.25
Figure 5.1	Chemical structures of (a) 2-hydroxyethyl acrylate (HEA); (b) *N, N'*-methylene-bisacrylamide (BIS); (c) Polyhydroxyethylacrylate (PHEA). The circles indicate the affected stretching double bonds of co-monomers likely to be broken down into stretching single bonds during polymerization.	5.5

Figure 5.2	Chemical structures of (a) 2-Hydroxyethyl Methacrylate (HEMA); (b) *N, N'*-methylene-bisacrylamide (BIS); (c) Polyhydroxyethylmethacrylate (PHEMA). The circles indicate the affected stretching double bonds of co-monomers likely to be broken down into stretching single bonds during polymerization.	5.6
Figure 5.3	Initiation of chemical structure (a) HEA; (b) HEMA; (c) *N, N'*-methylene-bisacrylamide (BIS); (d) propagation of PHEAG; (e) propagation of PHEMAG.	5.7
Figure 5.4	Normalised Raman intensity of C-C stretching showing the formation of PHEAG at (a) 2%, (b) 3%, (c) 4%, and (4) 5% HEA and for different BIS concentrations at 5 mM ascorbic acid.	5.10
Figure 5.5	Normalised Raman intensity of C-C stretching showing the formation of PHEAG at (a) 2%, (b) 3%, (c) 4%, and (4) 5% HEA and for different BIS concentrations at 10 mM ascorbic acid.	5.11
Figure 5.6	Normalised Raman intensity of C-C stretching showing the formation of PHEAG at (a) 2%, (b) 3%, (c) 4%, and (4) 5% HEA and for different BIS concentrations at 15 mM ascorbic acid.	5.12
Figure 5.7	Correlation between D_o and the initial concentration of HEA for different BIS concentration at (a) 5 mM, (b) 10 mM and (c) 15 mM ascorbic acid for the formation of PHEAG due to C-C stretching at 812 cm^{-1}.	5.14
Figure 5.8	Normalised Raman intensity of C-C stretching showing the formation of PHEAG at (a) 1%, (b) 2%, (c) 3%, and (4) 4% BIS and for different HEA concentrations at 5 mM ascorbic acid.	5.16
Figure 5.9	Normalised Raman intensity of C-C stretching showing the formation of PHEAG at (a) 1%, (b) 2%, (c) 3%, and (4) 4% BIS and for different HEA concentrations at 10 mM ascorbic acid.	5.17
Figure 5.10	Normalised Raman intensity of C-C stretching showing the formation of PHEAG at (a) 1%, (b) 2%, (c) 3%, and (4) 4% BIS and for different HEA concentrations at 15 mM ascorbic acid.	5.18

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 (4) 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 (4) 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 (4) 4% BIS and for different HEA concentrations at 15 mM ascorbic acid.	5.29
Figure 5.19	Correlation between D_o 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 (4) 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 (4) 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 (4) 5% HEA and for different BIS concentrations at 15 mM ascorbic acid.	5.40
Figure 5.27	Correlation between D_o 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 (4) 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 (4) 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 (4) 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
Figure 5.36	Normalised Raman intensity of C-C stretching showing the formation of PHEMAG at (a) 1%, (b) 2%, (c) 3%, and (4) 4% BIS and for different HEMA concentrations at 5 mM ascorbic acid.	5.54
Figure 5.37	Normalised Raman intensity of C-C stretching showing the formation of PHEMAG at (a) 1%, (b) 2%, (c) 3%, and (4) 4% BIS and for different HEMA concentrations at 10 mM ascorbic acid.	5.55