



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS OF HYDROGELS BY FREE RADICAL
COPOLYMERIZATION OF SAGO STARCH OR CHITOSAN AND
HYDROPHILIC VINYL MONOMERS AND THEIR
CHARACTERIZATIONS**

ABDUEL MAJID K. NAJJAR

FSAS 2002 50

**SYNTHESIS OF HYDROGELS BY FREE RADICAL
COPOLYMERIZATION OF SAGO STARCH OR CHITOSAN AND
HYDROPHILIC VINYL MONOMERS AND THEIR
CHARACTERIZATIONS**

By

ABDUEL MAJID K. NAJJAR

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

June 2002



DEDICATION

To the souls of my beloved father and grandfather in the heavens (Khalifa and Emhemmed), who regretfully did not live to see this work, which resulted from their gift of many years of love, encourage and support to me.

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

**SYNTHESIS OF HYDROGELS BY FREE RADICAL
COPOLYMERIZATION OF SAGO STARCH OR CHITOSAN AND
HYDROPHILIC VINYL MONOMERS AND THEIR
CHARACTERIZATIONS**

By

ABDUEL MAJID K. NAJJAR

June 2002

Chairman: Professor Wan Md. Zin Wan Yunus, Ph.D.

Faculty: Science and Environmental Studies

Sago starch was incorporated in the synthesis of polymer gel networks by free radical crosslinking copolymerization in an aqueous solution using potassium persulfate as an initiator. Three different monomers (2-acrylamido-2-methylpropanesulfonic acid (AMPS), acrylic acid and methyl-2-acrylamido-2-methoxyacetate (MAMOA)) with a common crosslinking agent (*N,N'*-methylenebisacrylamide (NMBA)) were used to synthesize these gel networks. A series of studies was carried out to evaluate and optimize the effect of the reaction parameters such as the amount of the monomer, the crosslinking agent and sago starch as well as liquor volume on the polymer gel networks yield. It was found that the percentages of gelation fraction and total conversion were dependent on these parameters.

The swelling behaviors of these polymeric gel networks from the dry state in distilled water and NaCl solutions of different concentration were also investigated. The maximum saturated water absorbency of 440 g H₂O/g dry gel was obtained for the gel network prepared from 1 g sago starch, 38.16×10^{-3} mol AMPS and 1.29×10^{-3} mol NMBA in the presence of 45 mL liquor volume. The absorbency of the hydrogel networks in the salt solutions was affected by the salt concentrations and the charge number of cations and anions.

The swelling capacity of the sago starch-poly(acrylic acid)-poly(NMBA) gel network could be increased by saponification with NaOH solution, and the saponification conditions (treatment temperature, treatment period and concentration of NaOH solution) were important in determining the water absorbency.

Polymeric materials from sago starch, acrylic acid and NMBA were synthesized in cylindrical form to evaluate their potential use as a water soluble drug carrier. The effects of the amount of sago starch, acrylic acid and NMBA during polymerization on the swelling behavior as well as on the loading and releasing of MgSO₄ were investigated. The amount of salt loaded was found to be dependent upon the concentration of MgSO₄ solution. The release profile of MgSO₄ can be controlled by varying the amount of poly(acrylic acid) and the crosslinking density in the gel network.

Preparation of the hydrogels by homogeneous grafting of MAMOA onto sago starch in an aqueous solution using potassium persulfate as an initiator was also investigated. The effects of the reaction conditions have been studied in term of percentage of grafting (% *G*). The optimum polymerization temperature and reaction period were found to be 50 °C and 2 hr, respectively. The % *G* was increased with the increase of the amount of monomer but decreased with the increase of amount of sago starch. The highest % *G* of about 62 % was obtained when the copolymerization reaction was carried out for 2 hr at 50 °C using 0.74×10^{-3} mol of potassium persulfate and 11.55×10^{-3} mol of MAMOA with 2 g of sago starch in 35 mL distilled water.

2-Acrylamido-2-methylpropanesulfonic acid (AMPS) has also been successfully grafted onto chitosan from homogenous solution using potassium persulfate as a redox initiator. The maximum percentage of grafting was about 180% under the optimum conditions (1% V/V acetic acid, 50 °C reaction temperature, 10 min chitosan-potassium persulfate mixing period, 0.37×10^{-3} mol of potassium persulfate and 28.96×10^{-3} mol of AMPS). The grafted chitosan was insoluble in the acid solution used for the grafting.

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

**SINTESIS HIDROGEL MELALUI PENGKOPOLIMERAN RADIKAL
BEBAS KANJI SAGU ATAU KITOSAN DAN MONOMER VINIL
HIDROFILIK DAN PENCIRIANNYA**

Oleh

ABDUEL MAJID K. NAJJAR

Jun 2002

Pengerusi: Profesor Wan Md. Zin Wan Yunus, Ph.D.

Fakulti: Sains dan Pengajian Alam Sekitar

Kanji sagu telah digunakan dalam penyediaan polimer rangkaian hidrogel secara pempolimeran radikal bebas dalam larutan akueus menggunakan kalium persulfat sebagai pemula. Tiga monomer yang berbeza (asid-2-akrilamido-2-metilpropanasulfonik (AMPS), asid akrilik dan metil-2-akrilamido-2-metoksiasetat (MAMOA) dengan agen perangkai silang (N,N'-metilenabisakrilamida (NMBA)) digunakan untuk menyedia rangkaian gel tersebut. Kajian secara sistematik telah dilakukan bagi menentukan keadaan optimum yang mempengaruhi tindak balas pempolimeran seperti kuantiti monomer, agen perangkai silang dan kanji sagu serta pelarut terhadap hasil polimer rangkaian hidrogel. Didapati peratus pengelatinan dan peratus petukaran total bergantung kepada parameter ini.

Perlakuan pengembangan rangkaian gel yang kering dikaji dalam air dan juga larutan NaCl dengan kepekatan yang berbeza. Didapati penyerapan tepu air

maksima adalah 440 g air/ g gel kering bagi gel kering yang disediakan daripada 1.00 g kanji sagu, 38.16×10^{-3} mol dan 1.29×10^{-3} mol NMBA dalam 45 mL pelarut. Kesan terhadap kepekatan, cas kation dan cas anion terhadap penyerapan rangkaian hidrogel dalam salin juga dikaji. Penyerapan rangkaian hidrogel dalam larutan garam bergantung kepada kepekatan garam serta cas kation dan cas anion.

Kapasiti pengembangan rangkaian gel kanji sagu-poli(asid akrilik)-poli (NMBA) boleh ditingkatkan melalui disaponikasikan dengan larutan NaOH. Kesan terhadap keadaan saponikasi (suhu rawatan, masa rawatan dan kepekatan larutan NaOH) amat penting bagi menentukan penyerapan air.

Bahan polimer dari kanji sagu, asid akrilik dan NMBA disintesis dalam bentuk selinder unjuk kajian penggunaannya sebagai bahan pembawa dadah larut-air. Kesan kuantiti kanji sagu, asid akrilik dan NMBA semasa pempolimeran terhadap perlakuan pengembangan serta pemuatan dan pembebasan MgSO_4 juga dikaji. Akaun garam yang dapat dimuatkan didapati bergantung kepada larutan MgSO_4 . Profil pelepasan MgSO_4 dapat dikawal dengan mengubah akaun poli(asid akrilik) dan ketumpatan rangkai silang dalam rangkaian hidrogel.

Kajian ini juga melibatkan penyediaan hidrogel secara pencangkukan homogen metil-2-akrilamido-2-metoksiasetat (MAMOA) ke atas kanji sagu dalam larutan akueus menggunakan kalium persulfat sebagai pemula. Kesan terhadap keadaan tindak balas dikaji berdasarkan peratus cangkukan (% G). Suhu optimum bagi pempolimeran dan masa tindak balas masing-masing adalah 50 °C dan 2

jam. Peratus cangkukan bertambah dengan pertambahan amaun monomer tetapi berkurang dengan pertambahan amaun kanji sagu. Peratus cangkukan maksima adalah 62% apabila tindak balas pengkopolimeran dilakukan selama 2 jam pada suhu 50 °C menggunakan 0.74×10^{-3} mol kalium persulfat, 11.55×10^{-3} mol MAMOA dengan 2 g kanji sagu dan 35 mL air suling.

Asid 2-akrilamido-2-metipropanasulfonik (AMPS) juga berjaya dicangkukkan ke atas kitosan dalam larutan homogen menggunakan kalium persulfat sebagai pemula redoks. Peratus cangkukan maksima adalah 180% pada keadaan optimum (1% V/V asid asetik, suhu tindak balas 50°C, masa campuran kitosan dengan kalium persulfat 10 min, kuantiti kalium persulfat 0.37×10^{-3} mol dan kuantiti AMPS 28.96×10^{-3} mol). Kitosan yang dicangkukkan tidak larut dalam larutan asid yang diguna untuk pengcangkukan.

ACKNOWLEDGMENTS

I would like to thank Allah (S.W.T.) for giving me this opportunity to continue my study and giving me the patience and perseverance to successfully complete my Ph.D. thesis.

I would like also to express my sincere thanks and profound appreciation to the chairman of my supervisory committee, Prof. Dr. Wan Md. Zin Wan Yunus for his guidance and discussion. Under his supervision, I have received heaps of assistance without which this work could not have been done. I am also indebted to Assoc. Prof. Dr. Mansor Bin Ahmad and Assoc. Prof. Dr. Mohamad Zaki AB. Rahman my co-supervisors for their help and guidance. My appreciation and honest thanks to all staff members from Department of Chemistry.

Completing this research work owes much to my wife Khirya, for her encouragement and understanding, which made life easy throughout my study. I am very grateful to her. Last but not least, I would like to acknowledge my intimate and loving children, Heyam, Weam, Narmin and Nur-Elhuda who also donated much time as they exerted great efforts concentrating on their own lessons. Special thanks to my sons Mohamed and Haytem, who also donated great patience and much time, that would have otherwise been spent playing with them during the course of my studies. My salute to all of them for their patience and understanding. My special appreciation and gratitude go on particularly to my

mother in Libya, for being a source of encouragement, and always ready to offer a helping hand.

Finally, most profound thanks go to the Libyan government represented by General Secretariat of Education for their financial support and to University Putra Malaysia for giving me this opportunity to study in their prestigious and reputed institute.

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSRAK	vi
ACKNOWLEDGEMENTS	xi
DECLARATION FORM	xiii
LIST OF TABLES	xix
LIST OF FIGRURES	xxi
LIST OF ABBREVIATIONS	xxxi
 CHAPTER	
 1 INTRODUCTION	 1
1.1 Background of the Study	1
1.2 General Background	6
1.2.1 Graft Copolymer	6
1.2.2 Hydrogel	7
1.2.3 Interpenetrating Polymer Network	8
1.2.4 Swelling Property of Hydrogel	11
1.2.5 Application of Hydrogel as Drug Delivery System	12
1.3 Strategy of the Study	13
1.4 The Main Objectives of the Work	14
1.5 Organization of Chapters	15
 2 LITREATURE REVIEW	 17
2.1 Graft Copolymerization	17
2.2 Graft Copolymerization Reaction for Polysaccharides	18
2.3 Persulfate Initiation	20
2.4 Graft Copolymerization onto Chitosan	21
2.5 Synthesis and Properties of Superabsorbents	26
2.6 Swelling of Hydrogels	35
2.7 Analysis of the Hydrogel Swelling Process	36
2.8 Theory of Swelling Equilibrium	37
2.9 Some Applications of Superabsorbents	41
2.10 Drug Delivery Systems	43
2.11 Summary of Literature Review	46
 3 MATERIALS AND METHODS	 48
3.1 Sago Starch	48
3.2 Chitosan	48



3.3	2-Acrylamido-2-Methylpropanesulfonic Acid (AMPS)	48
3.4	Acrylic Acid	49
3.5	Methyl-2-Acrylamido-2-Methoxyacetate (MAMOA)	50
3.6	<i>N,N'</i> -Methylenebisacrylamide (NMBA)	50
3.7	Potassium Persulfate	51
3.8	Water	51
3.9	Other Chemicals	52
3.10	Gelatinization of Sago Starch	53
3.11	Synthesis of Poly(AMPS) Grafted Chitosan	53
3.12	Synthesis of Sago Starch-Poly(AMPS)-Poly(NMBA) Gel Network	54
3.13	Synthesis of Sago Starch-Poly(Acrylic Acid)- Poly(NMBA) Gel Network	55
3.14	Synthesis of Poly(MAMOA) Grafted Sago Starch	56
3.15	Synthesis of Sago Starch-Poly(MAMOA)- Poly(NMBA) Gel Network	57
3.16	Syntheses of Cylindrical Gel Network of Sago Starch- Poly(Acrylic Acid)-Poly(NMBA)	57
3.17	Purification of Copolymer Materials.	59
3.18	FTIR Spectroscopy	59
3.19	Calculation of the Percentage of Grafting	59
3.20	Calculation of the Percentage of Gelation Fraction	60
3.21	pH Titration and Calculation of the Percentage of Total Conversion	60
3.22	Thermogravimetric Analysis (TGA)	61
3.23	Differential Scanning Calorimetric (DSC)	61
3.24	Swelling Kinetics Measurements	62
3.25	Saturated Water Absorbency Measurements	63
3.26	Saturated Absorbency Measurements in NaCl Solution	63
3.27	Saturated Absorbency Measurements in Various Salt Solutions Analysis	63
3.28	Saturated Absorbency Measurements in Acetone-Water Solvent	64
3.29	Determination of the Percentage of Water Content	64
3.30	Saponification of Gel Network	65
3.31	Swelling Measurements of Cylindrical Form Gel Networks	65
3.32	Swelling Measurements in pH Buffer Solution	66
3.33	Swelling Measurements in Acetone-Water Mixture	66
3.34	Thermal Effect on the Water Retained	66
3.35	Application of Hydrogel For Salt Release	67
3.35.1	Salt Loading	67
3.35.2	Salt Release	67
4	RESULTS AND DISCUSSION	69
4.1	Sago Starch-Poly(AMPS)-Poly(NMBA) Gel Network	69

4.1.1	General Consideration of Synthesis Gel Network	69
4.1.2	Proposed Polymerization Mechanism.	72
4.1.3	Effect of the Copolymerization Temperature	75
4.1.4	Effect of the Amount of Monomer	77
4.1.5	Effect of the Amount of Crosslinking Agent	79
4.1.6	Effect of the Amount of Sago Starch	81
4.1.7	Effect of the Liquor Volume	83
4.1.8	Thermal Degradation	85
4.1.9	Swelling Behavior of Sago Starch-Poly (AMPS)-Poly(NMBA) Gel Network in Distilled Water	89
4.1.10	Effect of the Amount of Monomer on Saturated Water Absorbency	93
4.1.11	Effect of the Amount of Crosslinking Agent on Saturated Water Absorbency	98
4.1.12	Effect of the Amount of Sago Starch on Saturated Water Absorbency	100
4.1.13	Effect of the Liquor Volume on Saturated Water Absorbency	101
4.1.14	Swelling Behavior of Sago Starch-Poly(AMPS)-Poly(NMBA) Gel Network in Salt Solution	103
4.1.15	Swelling Behavior of Sago Starch-Poly(AMPS)-Poly(NMBA) Gel Network in Acetone-Water Solvent	112
4.1.16	Thermal Effect on the Water Retained	114
4.2	Poly(AMPS) Grafted Chitosan	115
4.2.1	Synthesis of Poly(AMPS) Grafted Chitosan	116
4.2.2	Fourier Transform Infrared Analysis (FTIR)	118
4.2.3	Effect of the Reaction Variables on Grafting	121
4.2.4	Effect of Chitosan-Potassium Persulfate Contact Time	121
4.2.5	Effect of the Reaction Temperature	122
4.2.6	Effect of the Amount of Monomer	124
4.2.7	Effect of the Amount of Initiator	126
4.2.8	Effect of the Acetic Acid Concentration	128
4.3	Sago Starch-Poly(acrylic acid)-Poly(NMBA) Gel Network	129
4.3.1	Preparation of Gel Network	130
4.3.2	Effect of the Amount of Potassium Persulfate	131
4.3.3	Effect of the Amount of Acrylic Acid	133
4.3.4	Effect of the Amount of NMBA	135
4.3.5	Effect of the Amount of Sago Starch	137
4.3.6	Effect of the Liquor Volume	139
4.3.7	Effect of NaOH	141
4.3.8	DSC Analysis of Gel Network	143
4.3.9	Swelling Behavior of Sago Starch-Poly(acrylic acid)-poly(NMBA) Gel Networks	146

4.3.10	Time Dependence of Water Absorption	148
4.3.11	Effect of the Amount of Acrylic Acid on %EWC	149
4.3.12	Effect of the Amount of NMBA on %EWC	151
4.3.13	Effect of the Amount of Sago Starch on %EWC	153
4.3.14	Effect of the Liquor Volume on %EWC	155
4.3.15	Effect of NaOH During Copolymerization on Water Absorbency	156
4.3.16	Swelling of Sago Starch-Poly(acrylic acid)-Poly(NMBA) Gel Networks in NaCl Solution	159
4.3.17	Swelling of Neutralized Sago Starch-Poly(acrylic acid)-Poly(NMBA) in NaCl Solution	164
4.3.18	Alkaline Treatment of Sago Starch-Poly(acrylic acid)-Poly(NMBA) Gel Network	165
4.3.19	Effect of Treatment Temperature	166
4.3.20	Effect of NaOH Concentration	168
4.3.21	Effect of Treatment Period	169
4.4	Sago Starch Grafted Poly(MAMOA)	171
4.4.1	Polymerization Mechanism	171
4.4.2	Evidence for Grafting	172
4.4.3	Effect of the Polymerization Temperature	175
4.4.4	Effect of the Polymerization Period	177
4.4.5	Effect of the Amount of Initiator	178
4.4.6	Effect of the Amount of Monomer	180
4.4.7	Effect of the Amount of Sago Starch	181
4.4.8	Effect of the Liquor Volume	183
4.5	Sago Starch-Poly(MAMOA)-Poly(NMBA) Gel Network	185
4.5.1	Preparation of Gel Network	185
4.5.2	Effect of the Reaction Temperature	186
4.5.3	Effect of the Reaction Period	186
4.5.4	Effect of the Amount of Initiator	189
4.5.5	Effect of the Amount of Monomer	191
4.5.6	Effect of the Amount of Crosslinking Agent	193
4.5.7	Effect of the Amount of Sago Starch	194
4.5.8	Effect of the Liquor Volume	196
4.5.9	Swelling Behavior of Sago Starch-Poly(MAMOA)-Poly(NMBA) Gel Network	197
4.5.10	Effect of the Amount of Monomer on Saturated Absorbency	198
4.5.11	Effect of the Crosslinking Agent on Water Absorbency	202
4.5.12	Effect of the Sago Starch on Water Absorbency	204
4.5.13	Effect of the Liquor Volume on Water Absorbency	206
4.6	Cylindrical Gel Network of Sago Starch-Poly(Acrylic Acid)-Poly(NMBA)	208

4.6.1	General Consideration of the Preparation	208
4.6.2	Swelling Kinetics in Distilled Water	210
4.6.3	Saturated Water Absorbency	216
4.6.4	Swelling Behavior in Buffer Solution of Different pH	219
4.6.5	Swelling in Acetone-Water Volume Ratio	222
4.6.6	Salt Release Study	224
4.6.7	Salt Loading	225
4.6.8	Salt Release	228
5	CONCLUSIONS AND FURTHER RECOMMENDATIONS	241
5.1	Conclusions	241
5.2	Recommendations for Further Research	248
	REFERENCES	251
	PUBLICATION FROM THIS THESIS	B.1
	BIODATA	B.2

LIST OF TABLES

Table	Page
3.1	The rest of the chemical used in the study 52
4.1	The chemical compositions and liquor volume for hydrogel networks preparation 92
4.2	Effect of the amount of AMPS in the feed composition on initial absorption rate, time required to reach saturated absorbency and swelling rate 97
4.3	Effect of the amount of sago starch in feed composition on initial absorption and swelling rate of gel network of different amounts of sago starch in NaCl solution of different concentrations 105
4.4	Saturated absorbency (Q) of sago starch-poly(AMPS)-poly(NMBA) hydrogel network sample G12 in solutions of different cations with common anion 110
4.5	Saturated absorbency (Q) of sago starch-poly(AMPS)-poly(NMBA) hydrogel network sample G12 in solutions of different anions with common cation 112
4.6	Characteristic IR peaks of chitosan (absorption bands of chitosan) 119
4.7	Effect of chitosan-potassium persulfate mixing period on the percentage of grafting (% G) [chitosan = 0.6135 g, initiator = 1.85×10^{-3} mol, AMPS = 65×10^{-3} mol, acetic acid = 2% V/V] 122
4.8	The T_g s of the sago starch and sago starch-poly(acrylic acid)-poly(NMBA) gel networks 146
4.9	The chemical compositions and liquor volume for hydrogel networks preparation 149
4.10	The chemical compositions and liquor volume for hydrogel network preparation 199
4.11	The chemical compositions during copolymerization and the percentage of gelation fraction of gel networks [potassium persulfate = 0.37×10^{-3} mol, volume of distilled water = 0.37×10^{-3} mol, polymerization temperature = 60 °C and reaction period = 3 hr] 210



4.12	The calculated values of n for the hydrogel networks swollen in distilled water	215
4.13	Saturate absorbency of hydrogel networks in buffer solution of different pH [swelled for 7 days in pH 4.00, pH 7.00 and pH 10.00]	220
4.14	The weights of dry gel networks, salt in the loaded dry gel networks and percentages of load of after swollen in different concentration of MgSO_4 for 7 days	226
4.15	The calculated values of release index (n)	237

LIST OF FIGURES

Figure		Page
2.1	A Repeating Unit of Chitosan	22
2.2	Structure of Starch Units, (a) Amylose and (b) Amylopectin Components	26
4.1	The IPN Structure (solid line denotes the grafted crosslinked poly(AMPS) onto starch and dotted line presents the crosslinked poly(AMPS)	72
4.2	Effect of Reaction Temperature on the Percentages of Gelation Fraction (●) and Total Conversion (▲) [starch= 1.00 g, $K_2S_2O_8 = 0.37 \times 10^{-3}$ mol, AMPS= 9.65×10^{-3} mol, NMBA= 1.29×10^{-3} mol, liquor volume= 30 mL]	76
4.3	Effect of the Amount of Monomer (AMPS) in Feed Composition on the Percentages of Gelation Fraction (●) and Total Conversion (▲) [starch= 1.00 g, temperature= 60 °C, $K_2S_2O_8 = 0.37 \times 10^{-3}$ mol, NMBA= 1.29×10^{-3} mol, liquor volume= 30 mL]	79
4.4	Effect of the Amount of Crosslinker (NMBA) in the Feed Composition on the Percentages of Gelation Fraction (●) and Total Conversion (▲) [starch= 1.00 g, temperature= 60 °C, $K_2S_2O_8 = 0.37 \times 10^{-3}$ mol, AMPS= 38.61×10^{-3} mol, liquor volume= 30 mL]	81
4.5	Effect of the Amount of Sago Starch in the Feed Composition on the Percentages of Gelation Fraction (●) and Total Conversion (▲) [temperature= 60 °C, $K_2S_2O_8 = 0.37 \times 10^{-3}$ mol, AMPS= 10.31×10^{-3} mol, NMBA= 1.29×10^{-3} mol, liquor volume= 30 mL]	82
4.6	Effect of the Liquor Volume on the Percentages of Gelation Fraction (●) and Total Conversion (▲) [starch= 1.00 g, temperature= 60 °C, $K_2S_2O_8 = 0.37 \times 10^{-3}$ mol, AMPS= 38.61×10^{-3} mol, NMBA= 1.29×10^{-3} mol]	85
4.7	TGA Curves of (A) Starch, (B) Crosslinked Poly(AMPS) and (C) Sago Starch-Poly(AMPS)-Poly(NMBA) IPN [starch= 4.00 g, temperature= 60 °C, $K_2S_2O_8 = 0.37 \times 10^{-3}$ mol, AMPS= 19.31×10^{-3} mol, NMBA= 1.29×10^{-3} mol]	86

4.8	The Relationship Between $-\ln(1/r)$ and $1/\theta$ of (A) Sago Starch, (B) Crosslinked Poly(AMPS) and (C) Starch-Poly(AMPS)-Poly(NMBA) IPN [sago starch= 4.00 g, temperature= 60 °C, $K_2S_2O_8= 0.37 \times 10^{-3}$ mol, AMPS= 19.31×10^{-3} mol, NMBA= 1.29×10^{-3} mol]	88
4.9	A Photographic Print of Dry and Swollen Hydrogel Networks	90
4.10	A Photographic Print of Swollen Hydrogel of High Sago Starch Content	91
4.11	Swelling Dynamics of Sago Starch-Poly(AMPS)-Poly(NMBA) Hydrogel Networks Prepared from Different Amounts of AMPS G1(■), G2(◆), G3(▲) and G14(●) in Distilled Water [sago starch = 1.00 g, NMBA = 1.29×10^{-3} mol]	94
4.12	Effect of the Amount of Monomer (AMPS) in the Feed Composition on Saturated Water Absorbency of Hydrogel Network [sago starch = 1.00 g, NMBA = 1.29×10^{-3} mol, liquor volume = 30 mL]	97
4.13	Effect of the Amount of Crosslinking Agent (NMBA) in the Feed Composition on Saturated Water Absorbency of Gel Network [sago starch = 1.00 g, AMPS = 38.16×10^{-3} mol, liquor volume = 30 mL]	99
4.14	Effect of the Amount of Sago Starch in the Feed Composition on Saturated Water Absorbency of Gel Network [AMPS = 19.31×10^{-3} mol, NMBA = 1.29×10^{-3} mol, liquor volume = 30 mL]	101
4.15	Effect of Liquor Volume of Polymerization on Saturated Water Absorbency of Gel Network [sago starch = 1.00 g, AMPS = 38.16×10^{-3} mol, NMBA = 1.29×10^{-3} mol]	102
4.16	Swelling Dynamics of Gel Networks Prepared from Different Amounts of Sago Starch G10(●), G11(▲) and G12(■) in 0.01 M NaCl Solutions [AMPS = 19.31×10^{-3} mol, NMBA = 1.29×10^{-3} mol, liquor volume = 30 mL]	104
4.17	Swelling Dynamics of Gel Networks Prepared from Different Amounts of Sago Starch G10(●), G11(▲) and G12(■) in 0.10 M NaCl Solutions [AMPS = 19.31×10^{-3} mol, NMBA = 1.29×10^{-3} mol, liquor volume = 30 mL]	105

4.18	Swelling Dynamics of Gel Networks Prepared from Different Amounts of Sago starch G10 (●), G11 (▲) and G12 (■) in 1.00 M NaCl Solutions [AMPS = 19.31×10^{-3} mol, NMBA = 1.29×10^{-3} mol, liquor volume = 30 mL]	106
4.19	Saturated Absorbency for Various Hydrogel Network of Different Amounts of Monomer (AMPS) During Polymerization in Various Concentrations of NaCl Solution. 0.01 M (●), 0.05 M (▲), 0.10 M (◆), 0.50 M (■), 1.00 M (○) [sago starch = 1.00 g, NMBA = 1.29×10^{-3} mol, liquor volume = 30 mL]	107
4.20	Saturated Absorbency for Various Hydrogel Networks of Different Amounts of Sago Starch During Polymerization in Various Concentrations of NaCl Solution. 0.01 M (●), 0.05 M (▲), 0.10 M (◆), 0.50 M (■), 1.00 M (○) [AMPS = 19.31×10^{-3} mol, NMBA = 1.29×10^{-3} mol, liquor volume = 30 mL]	109
4.21	Effect of Solvent Compositions on the Saturated Absorbency of Sago Starch-Poly(AMPS)-Poly(NMBA) Hydrogel Networks G5 (●) and G12 (▲)	113
4.22	Thermal Effect at 70 °C on the Water Retention in Sago Starch-Poly(AMPS)-Poly(NMBA) Hydrogel Network Samples G12 (●) and G5 (▲)	115
4.23	The Mechanism of Graft Copolymerization of AMPS onto Chitosan	117
4.24	Traces of FTIR Spectra of (A) Chitosan and (B) Grafted Chitosan	120
4.25	Effect of Reaction Temperature on the Percentage of Grafting (%G) [chitosan 0.6135 g, initiator 1.85×10^{-3} mol, AMPS 9.65×10^{-3} mol, acetic acid 2% V/V]	123
4.26	Effect of the Amount of AMPS on the Percentage of Grafting (%G) [chitosan = 0.6135 g, reaction temperature = 50 °C, initiator = 1.85×10^{-3} mol, acetic acid = 2% V/V]	125
4.27	Effect of Amount of Initiator on the Percentage of Grafting (%G) [chitosan = 0.6135 g, reaction temperature = 50 °C, AMPS = 28.96×10^{-3} mol, acetic acid = 2% V/V]	127
4.28	Effect of Acetic Acid on the Percentage of Grafting (%G) [chitosan = 0.6135 g, reaction temperature = 50 °C, initiator = 0.37×10^{-3} , AMPS = 28.96×10^{-3} mol]	128

4.29	Effect of the Amount of Potassium Persulfate on the Percentage of Gelation Fraction [sago starch = 3.00 g, reaction temperature = 60 °C, liquor volume = 50 mL, acrylic acid = 72.86×10^{-3} mol, crosslinker = 1.95×10^{-3} mol]	132
4.30	Effect of the Amount of Acrylic Acid on the Percentage of Gelation Fraction [sago starch = 3.00 g, volume of H ₂ O = 50 mL, reaction temperature = 60 °C, K ₂ S ₂ O ₈ = 0.93×10^{-3} mol, crosslinker = 1.95×10^{-3} mol]	135
4.31	Effect of the Amount of Crosslinker on the Percentage of Gelation Fraction [sago starch = 3.00 g, liquor volume = 50 mL, reaction temperature = 60 °C, K ₂ S ₂ O ₈ = 0.93×10^{-3} mol, acrylic acid = 72.86×10^{-3} mol]	137
4.32	Effect of the Amount of Sago Starch on the Percentage of Gelation Fraction [volume of H ₂ O = 50 mL, the reaction temperature = 60 °C, Amount of K ₂ S ₂ O ₈ = 0.93×10^{-3} mol, acrylic acid = 72.86×10^{-3} mol, crosslinker = 1.95×10^{-3} mol]	139
4.33	Effect of the Liquor Volume on the Percentage of Gelation Fraction [sago starch = 3.00 g; reaction temperature = 60 °C; K ₂ S ₂ O ₈ = 0.93×10^{-3} mol; acrylic acid = 72.86×10^{-3} mol; cross linking agent = 1.95×10^{-3} mol]	140
4.34	Effect of the Amount of NaOH in the Reaction Mixture on the Percentage of Gelation Fraction [sago starch = 3.00 g, liquor volume = 50 mL, reaction temperature = 60 °C, K ₂ S ₂ O ₈ = 0.93×10^{-3} mol, acrylic acid = 72.86×10^{-3} mol, crosslinker = 1.95×10^{-3} mol]	142
4.35(A)	The DSC Thermograms of Sago Starch (sample G1) and Starch-Poly(acrylic acid)-Poly(NMBA) Gel Networks (sample G3)	144
4.35(B)	The DSC Thermograms of Starch-Poly(acrylic acid)-Poly(NMBA) Gel Networks samples G2 and G4	145
4.36	Swelling Dynamics of Sago Starch-Poly(acrylic acid)-Poly(NMBA) Gel Network of Different Amounts of Acrylic Acid During Polymerization H2 (●) and H5 (◆)	148
4.37	Swelling Behaviors of Hydrogel Networks of Different Amounts of Acrylic Acid [sago starch = 3.00 g, volume of H ₂ O = 50 mL, the reaction temperature = 60 °C, K ₂ S ₂ O ₈ = 0.93×10^{-3} mol, crosslinker = 1.95×10^{-3} mol]	150