UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLY(METHYL METHACRYLATE) GRAFTED SAGO STARCH

ISAM YASSIN MAHMOOD QUDSIEH

FSAS 1999 29

PREPARATION AND CHARACTERIZATION OF POLY(METHYL METHACRYLATE) GRAFTED SAGO STARCH

By

ISAM YASSIN MAHMOOD QUDSIEH

Thesis Submitted in Fulfilment of the Requirement
for the Degree of Master of Science in
the Faculty of Science and Environmental Studies
Universiti Putra Malaysia

June 1999

ACKNOWLEDGEMENTS

In The Name of ALLAH, The Most Merciful and Most Beneficent

I am very deeply grateful to ALLAH " A.W " for giving me the opportunity to study with strength and patience to complete this study. I would like to thank not just the few that inspired me, but also those who have accepted my mistakes and shortcomings. I am especially grateful to those who have taken time to look at the various stages of my study in spite of their busy schedule.

First and foremost, I wish to express my sincere gratitude and appreciation to the chairman of my supervisory committee Prof. Dr. Wan Md. Zin Wan Yunus, for his invaluable advice, comments, suggestions, help and personal guidance throughout my study. Also I wish to express my appreciation to my co-supervisor Dr. Hj Mohammad Zaki Abd Rahman for the fruitful discussion, continuous encouragement, help and guidance. I am also pleased to thank my co-supervisor Dr. Mansor bin Hj Ahmad for his constant support throughout my research work.

I am very much appreciative of the assistance given to me by the all the staff members of the Chemistry Department especially Assoc. Prof. Dr. Karen Badri for her suggestions, comments, kindness and encouragement.

I would like to express my most sincere and warmest gratitude to my father, mother, brothers, sisters, relatives and to the person I love for their prayers, loving, generous and moral inputs during my study. Words can not express my profound gratitude and special thanks to my sister Hanan who shared with me the away from home dreams during our stay together on UPM campus. My special thanks also go to Abeer Sahtout, Dr. Noha Yahya, Umme Ara and Gabby Setiowaty for their help, continuous encouragement and support. Not forgetting all my friends in Jordan-my beloved Home, for their correspondence and concern during the period of my stay in Malaysia. Special thanks go to the Embassy of Jordan in Kuala Lumpur and to all its employees. I would like in particular to thank the ambassador of the H.K.of Jordan Embassy in Kuala Lumpur Mr. Abdul Ilah Al-Kurdi and Mr Sudqi Al-Omoush for their help and moral support.

Special thanks go to my friend Abduel Majeed Al-Najjar for his untiring encouragement, help and guidance. I would like to particularly thank Dr. Dau Khoshaim, Mrs Pushpamalar and Mr. Md Lutffor Rahman, and all the graduate and undergraduate students in the Chemistry Department for their friendly co-operation.

I would like to acknowledge those who supported me since my arrival in Malaysia, with special thanks to my friends Saleh Al-Khawaldeh, Faraj Abu Ilaiwi and Rafa Al-Qtaish, who supported me at all times. I would also like to thank my friend Moneef and his family for their kindness and moral support during my stay in Malaysia. Also I would like to convey my special thanks to my friends Ahmad and Atef Al-Khawaldeh, Malik Al Qudah, Hayel Al-Fuqara, Moh'd Abu Ghazleh, Ziyad Abo-Gaddorah, Moh'd Al-Smadi, Moh'd Al-Ghoul and Khalid Al-Zoa'abi for their encouragement and support. I am grateful to my friend Nasir (Biotechnology Department) for his help and kindness, and to all friends inside and outside UPM. Sincere thanks to all of them.

I would like to convey my sincere thanks and deepest gratitude to my close friend who stood beside me all the time. Indeed I am indebted to my brother Hasan Muqbil Al-Omoush for his help, support, encouragement and noble deeds.

Lastly, I would like to acknowledge Prof. Dr. Wan Md. Zin Wan Yunus for providing me a full scholarship during my study through his IRPA project supported by the Ministry of Science, Technology and Environment Malaysia.

TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PREPARATION AND CHARACTERIZATION OF POLY(METHYL METHCRYLATE) GRAFTED SAGO STARCH

By

ISAM YASSIN M. QUDSIEH

June 1999

Chairman: Professor Wan Md Zin Wan Yunus, PhD.

Faculty : Science and Environmental Studies

The graft copolymerization of poly(methyl methacrylate) (PMMA) onto sago starch (sago starch-g-PMMA) was carried out using ceric ammonium nitrate (CAN) and potassium persulfate (PPS) as initiators. PMMA was first grafted onto sago starch using CAN as an initiator under nitrogen gas atmosphere. The maximum percentage of grafting (%G) was determined to be 246% when the optimum conditions (reaction temperature: 70 ^{0}C, reaction period: 2 hrs, the amount of CAN: 2.0 mmoles, the amount of nitric acid: 0.4 mmoles, and the amount of methyl methacrylate (MMA): 141 mmoles). When PPS was used as an initiator, the maximum %G achieved was 90%. The optimum conditions for this initiator were as follows: reaction

temperature: 50 ^{0}C, the amount of monomer: 47 mmoles, the amount of PPS: 1.82 mmoles, and reaction period: 1.5 hr.

The copolymers produced were characterized by Fourier Transform Infrared Spectrophotometry (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The FTIR spectra of the copolymers clearly indicated the presence of characteristic peaks of PMMA and sago starch, which suggested that PMMA had been successfully grafted on the sago starch. DSC and TGA thermograms showed that the copolymerization products were made up of two different polymers.

The copolymers of various percentages of grafting were hydrolysed with 0.5 M hydrochloric acid and the viscosity measurements of PMMA produced were carried out using Ubbelohde viscometer. The average molecular weight ($\overline{M}_v$) of PMMA grafted onto the sago starch (246%G) prepared by using CAN as the initiator was 4.3×10^4, and from PMMA grafted sago starch (90%G) prepared by using PPS as the initiator was 1.3×10^4.

Biodegradability studies of sago starch-g-PMMA and sago starch were carried out by α-amylase enzyme. The rate of degradation

of sago starch was higher than the rate of degradation of sago starch-g-PMMA. Maximum biodegradation of the sago starch was achieved after 3 days of incubation, while for the copolymer was 7 days.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN KOPOLIMER POLI (METIL METAKRILAT)-KANJI SAGU

Oleh

ISAM YASSIN MAHMOOD QUDSIEH

Jun 1999

Pengerusi : Profesor Wan Md Zin Wan Yunus, PhD.

Fakulti : Sains dan Pengajian Alam Sekitar

Pengkopolimeran cangkuk poli (metil metakrilat) (PMMA) ke atas kanji sagu telah dikaji dengan menggunakan serium ammonium nitrat (CAN) dan kalium persulfat (PPS) sebagai pemula. Kajian dimulakan dengan mengcangkukkan PMMA ke atas kanji sagu dengan menggunakan CAN sebagai pemula tindak balas dilakukan dibawah atmosfera nitrogen. Peratus pencangkukan PMMA adalah 246% apabila tindak balas dijalankan dibawah keadaan optimum (suhu tindak balas: 70 ^{0}C, tempoh tindak balas: 2 jam, amaun CAN: 2.0 mmol, amaun asid nitrik: 0.4 mmol dan amaun metil metakrilat (MMA):141 mmol). Kalium persulfat telah digunakan sebagai pemula tindak balas yang kedua untuk mengcangkukkan PMMA ke atas kanji sagu juga di bawah atmosfera nitrogen. Peratus pengcangkukan tindak balas paling tinggi yang dicapai adalah 90% dengan menggunakan keadaan optimum suhu tindak balas: 50 ^{0}C, amaun monomer: 47 mmol, amaun kalium persufat: 1.82 mmol, dan tempoh tindak balas: 1.5 jam.

Pengcangkukkan PMMA ke atas kanji sagu telah dicirikan dengan teknik-teknik spektrofotometri inframerah (FTIR), kalorimetri pengimbasan pembezaan (DSC) dan analisis termogravimetri (TGA). Spektrum inframerah kopolimer jelas menunjukkan kehadiran puncak-puncak serapan PMMA dan kanji sagu. Ini menunjukkan pengkopolimeran telah berjaya dilakukan. Termogram-termogram DSC dan TGA juga menunjukkaan bahawa hasil pengkopolimeran mengandungi dua polimer yang berbeza.

Kopolimer ini telah dihidrolisis dengan menggunakan 0.5 M asid hidroklorik dan pengukuran kelikatan larutan PMMA yang dihasilkan telah dikaji untuk pelbagai peratus pengcangkukan dengan menggunakan viskometer Ubbelohde. Jisim molekul purata ($\bar{M}_v$) untuk kopolimer (246% pencangkukkan) kanji sagu-g-PMMA yang diperolehi dengan menggunakan CAN sebagai pemula tindak

balas adalah 4.3×10^4, dan untuk kanji sagu-g-PMMA (90% pencangkukan) yang diperolehi dengan menggunakan PPS sebagai pemula tindak balas adalah 1.3×10^4.

Biodegradasi ke atas kanji sagu-g-PMMA dan kanji sagu telah dijalankan dengan enzim α-amilase. Kadar penguraian untuk kanji sagu adalah lebih tinggi daripada kadar penguraian untuk kanji sagu-g-PMMA. Biodegradasi maksimum bagi kanji sagu dicapai selepas 3 hari manakala bagi kanji sagu-g-PMMA adalah 7 hari.

CHAPTER I

INTRODUCTION

Polysaccharides

Several hundred natural polysaccharides are currently known and become one of the richest and oldest reservoirs of structurally and functionally diverse biopolymers. Polysaccharides have played an essential role in the development of life on this planet, and constitute important members of the family of industrial water-soluble polymers. Innumerable uses have been established for carbohydrate polymers, and many new ones are constantly being discovered[1]. Polysaccharides present a variety of chemical structures, solubility, and molecular weights. Plant polysaccharides do not have uniform repeating-unit-type structures; rather they are polymolecular; i.e. their structures vary from molecule to molecule. In addition, the average structure can vary with the source and conditions under which the plant is grown[2].

Starch

Starch is one of the cheapest and most readily available of all natural polymers. Starch is a high polymer composed of repeating *1,4-α-D*-glucopyranosyl units (often called anhydroglucose units or simply AGU) and is, generally, a mixture of linear and branched components. The linear component, amylose, has a molecular weight of several hundred thousand; while the molecular weight of the branched amylopectin is of the order of several million. Branching in amylopectin occurs at C-6 of the glucopyranosyl unit. Starch occurs in living plants in the form of discrete granules, which range from about 5-40 μm in average diameter, depending on the source. Starch granules contain regions of crystallinity; and if starch is slurred in water at room temperature, its solubility is negligible, even though it is a hydrophilic polymer. Starch in this form will be designated here as unswollen. When the water slurry of starch is heated, hydrogen bonds are broken, and a measurable fraction of the starch is dissolved. The granules swell and lose their birefringence. If the temperature of the water slurry is raised near the boiling point, the granules will largely disintegrate to form a smooth dispersion[3].

Methyl Methacrylate

Methyl methacrylate (MMA) is a colourless volatile liquid monomer. Its boiling point is 101 ^{0}C and its density is 0.943. The monomer is slightly soluble in water, and in most organic solvents. It is readily polymerized by light, heat, ionizing radiation, and catalysts. MMA can be polymerised with other methacrylate esters and many other monomers. MMA is flammable and a dangerous fire risk. It is used for polymethacrylate resins and impregnation of concrete. The chemical structure of MMA is presented in Figure 1.

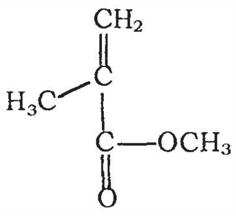
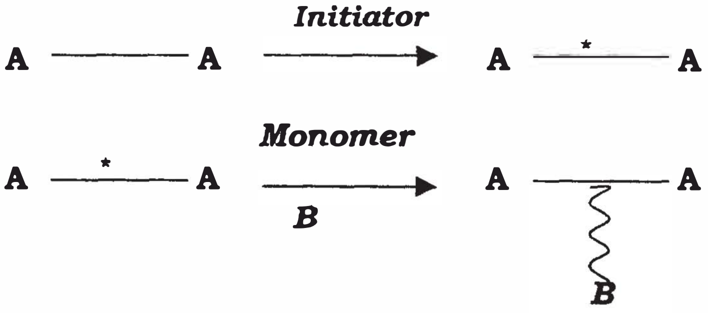


Figure 1: Chemical structure of methyl methacrylate

Graft and Free Radical Polymerization

Graft polymerization of monomers onto polysaccarides is one of the universal, effective and accessible methods of chemical modification of high molecular weight compounds. The polarity of polysaccharides stipulates for this purpose and the predominant application of radical graft polymerization. The advantage of radical polymerization is that it takes place in water media with a good yield of a final product. Methods of radical graft polymerization of monomers onto polysaccharides are based on the ability of the polysaccharides to become activated under the influence of mechanico-chemical, physical or chemical actions.

The graft copolymers can be synthesised by the reaction of polymer chains and different monomers by free radical initiation of the active sites on the polymer backbone (A) where the monomer (B) can be grafted, as illustrated in Scheme I. The free radical can also be produced by the radiation technique.



Scheme I: Grafting steps