VINYL-CHITOSAN MACROMONOMER: AN APPROACH FOR CONTROLLED STRUCTURE CHITOSAN



Ms. Kosum Samakrat

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science

The Petroleum and Petrochemical College, Chulalongkorn University
in Acadamic Partnership with

The University of Michigan, The University of Oklahoma,
and Case Western Reserve University

2002

ISBN 974-03-1615-8

Thesis Title:

Vinyl-Chitosan Macromonoemr: An Approach for Controlled

Structure Chitosan

By:

Ms. Kosum Samakrat

Program:

Polymer Science

Thesis Advisor:

Asst. Prof. Suwabun Chirachanchai

Assoc. Prof. David C. Martin

Accepted by the Petroleum and Petrochemical College, Chulalongkom University, in partial fulfillment of the requirements for the Degree of Master of Science

K. BunyahinT. College Director

(Assoc. Prof. Kunchana Bunyakiat)

Thesis Committee:

(Asst. Prof. Suwabun Chirachanchai)

(Assoc. Prof. David C. Martin)

(Dr. Ratana Rujiravanit)

Ratana Rujummit

Dr. Manis Nithitanakul)

ABSTRACT

4372009063 : POLYMER SCIENCE PROGRAM

Kosum Samakrat: Vinyl-Chitosan Macromonomer:

An Approach for Controlled Structure Chitosan.

Thesis Advisors: Asst. Prof. Suwabun Chirachanchai and

Assoc. Prof. David C. Martin, 47 pp. ISBN 974-03-1615-8

Keywords : Low molecular weight chitosan/ Acid hydrolysis/

Hydrochloric acid hydrolysis/ Chain degradation/ Water soluble low molecular weight chitosan/ Macromonomer/ Acrylic monomer/ Polymer chain layer/ Polymer gel/ Swelling

The preparation of water-soluble low molecular weight chitosan (LMCS) by acid hydrolysis is reported. The change in appearance from flake to powder and the reduction in molecular weight related to the hydrolysis time are clarified. The packing structure of low molecular weight chitosan observed from wide angle X-ray diffraction demonstrates the major change in reduction of intermolecular hydrogen bonding. Vinyl-chitosan macromonomer is originally proposed using the water-soluble low molecular weight chitosan reacted with acrylic acid monomer. The polymerization of acrylic acid and vinyl-chitosan macromonomer under the optimal molar ratio and reaction temperature are studied to clarify that the polymer obtained is a gel. The water absorption is applied to evaluate the performance of the gel product.

บทคัดย่อ

นางสาวโกสุม สมัครรัตน์: ไวนิล-ไคโตซาน แมคโครมอนอเมอร์: แนวทางไปสู่การควบ คุมโครงสร้างโคโตซาน (Vinyl-Chitosan Macromonomer: An Approach for Controlled Structure Chitosan) อ.ที่ปรึกษา: ผศ.คร.สุวบุญ จิรชาญชัย และ รศ.คร.เควิค ซี มาร์ติน (Assoc. Prof. David C. Martin), 47 หน้า ISBN 974-03-1615-8

รายงานนี้กล่าวถึงการเตรียมใคโตซานน้ำหนักโมเลกุลต่ำที่สามารถละลายน้ำได้เตรียมโดยการย่อยด้วยกรด และได้ให้ความกระจ่างเกี่ยวกับการเปลี่ยนสภาพจากแผ่นเล็กๆเป็นผงและการลดลงของน้ำหนักโมเลกุลซึ่งสัมพันธ์กับเวลาที่ใช้ในการย่อย การเปลี่ยนแปลงการเรียงตัวของใคโตซานน้ำหนักโมเลกุลต่ำศึกษาโดยเอกซ์เรย์ดิฟแฟรกชั่นสเปกโตรสโกรปี (X-ray Diffraction Spectroscopy) แสดงถึงการลดลงของพันธะไฮโดรเจนระหว่างโมเลกุลของใคโตซาน ไวนิล-ไคโตซานแมคโครมอนอเมอร์ถูกนำเสนอเป็นครั้งแรกโดยการผนวกของไคโตซานน้ำหนักโมเลกุล ต่ำที่ละลายน้ำได้และกรดอะคริลิคมอนอเมอร์ การศึกษาเงื่อนไขที่เหมาะสมสำหรับการทำปฏิกิริยาพอลิเมอร์ระหว่างกรดอะคริลิคและไวนิล-ไคโตซานแมคโครมอนอเมอร์ให้ความกระจ่างว่าพอลิเมอร์ที่ได้เป็นเจล สมบัติของผลิตภัณฑ์เจลประเมินโดยการศึกษาความสามารถในการดูดน้ำ

ACKNOWLEDGEMENTS

The author would like to express the sincerest appreciation to her Thai advisor, Asst. Prof. Suwabun Chirachanchai, who not only originated this research work, but also giving intensive suggestions, and vital help throughout this research work.

She wishes to thank Prof. Mitsuru Akashi and Prof. Kohji Tashio (Department of Macromolecular Science, Graduate School of Science, Osaka University, Japan) for their recommendations in the work. She would like to give a special thanks to Asst.Prof. Sanong Ekgasit (Department of Chemistry, Faculty of Science, Chulalongkorn University) for FTIR measurement. She would like to thank Seafresh Chitosan (Lab) Company Limited, Thailand, for supporting chitin-chitosan starting materials.

The author would like to thank all professors who have tendered invaluable knowledge to her at the Petroleum and Petrochemical College, Chulalongkorn University. She gratefully acknowledges her seniors, Ms. Rangrong Yoksan, Mr. Apirat Laobuthee, Ms. Bussarin Ksapabutr for their help, fruitful discussions and suggestions. She also would like to thank the college members, staffs, and her best friends at Petroleum and Petrochemical College for their helps and entertainment.

Finally, the deeply appreciation is dedicated to her family for the love, encouragement, understanding, and financial support.

TABLE OF CONTENTS

			PAGE
	Titl	e Page	i
	Abs	tract (in English)	iii
	Abs	tract (in Thai)	iv
	Ack	nowledgements	V
	Tab	le of Contents	vi
	List	of Schemes	viii
	List	of Figures	ix
CH	APTI	ER	
	I	INTRODUCTION	1
	П	WATER-SOLUBLE LOW MOLECULAR WEIGHT	CHITOSAN
		FROM HYDROCHLORIC AICD HYDROLYSIS	
		Abstract	8
		Introduction	9
		Experimental	11
		Results and Discussion	12
		Conclusions	14
		Acknowledgements	14
		References	14
	Ш	VINYL-CHITOSAN MACROMONOMER: AN APPRO	OACH FOR
		CONTROLLED STRUCTRUE CHITOSAN	
		Abstract	26
		Introduction	27
		Experimental	29
		Results and Discussion	31
		Conclusions	34

СНАРТІ	ER	PAGE	
	Acknowledgements References	34 34	
IV	CONCLUSIONS	44	
	REFERENCES	45	
	CURRICULUM VITAE	47	

LIST OF SCHEMES

SCHEME			PAGE
		Chapter I	
1	Scheme I		1
2	Scheme II		4
3	Scheme III		
4	Scheme IV		5
5	Scheme V		6
6	Scheme VI		7
		Chapter II	
1	Scheme I		16
2	Scheme II		17
		Chapter III	
1	Scheme I		36

LIST OF FIGURES

FIG	URE	PAGE
	Chapter I	
1	Structure of α -chitin: (a) bc projection, and (b) ab projection	2
	Chapter II	
1	Molecular weight of low molecular weight chitosan as a function of	19
	time.	
2	FTIR spectra of: (a) chitosan and chitosan obtained after hydrolysis	2()
	time for: (b) 3, (c) 6, (d) 9, and (e) 12 hrs.	
3	Degree of deacetylation as a function of time determined by: (a)	21
	FTIR: integral ratio of amide I band (1655 cm ⁻¹) and hydroxyl band	
	(3450 cm^{-1}) , and (b) $^{1}\text{H-NMR}$.	
4	¹ H-NMR of: (a) chitosan, and (b) low molecular weight chitosan.	22
5	X-ray diffractograms of: (a) chitosan and chitosan obtained after	23
	hydrolysis time for: (b) 3, (c) 6, (d) 9, and (e) 12 hrs.	
6	(a) TGA and DTA diagrams of chitosan, and (b) Degradation	24
	temperature of the products obtained from various hydrolysis times.	
7	Solubility of low molecular weight chitosan in 1% acetic acid as a	25
	function of time.	
	Chapter III	
1	FTIR spectra of: (a) low molecular weight chitosan, and (b) chitosan	38
	macromonomer.	
2	¹ H-NMR of: (a) low molecular weight chitosan, and (b) chitosan	39
	macromonomer.	
3	X-ray diffractograms of: (a) low molecular weight chitosan, and (b)	4()
	chitosan macromonomer.	

FIGURE		PAGE
4	FTIR spectra of LMCS-acrylic polymer at the molar ratios of LMCS macromonomer: acrylic acid for: (a) 1:20, (b) 1:30, (c) 1:40, and (d)	41
5	1:50. X-ray diffractograms of: (a) LMCS macromonomer, and LMCS-acrylic polymer at the molar ratios of LMCS macromonomer: acrylic	42
6	acid for: (b) 1:20, (c) 1:30, (d) 1:40, and (e) 1:50. Swelling percentage of: ★ chitosan, and LMCS-acrylic polymer at the molar ratio of LMCS macromonomer: acrylic acid for: (♠) 1:20,	43

(m) 1:30, (A) 1:40, and (O) 1:50.