# SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE LOW MOLECULAR WEIGHT POLYMERS

Thesis

**Submitted To** 

## THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

For The Degree of

Doctor of Philosophy In Applied Chemistry

> Submitted By **RENU SINGH**



Applied Chemistry Department Faculty of Technology & Engineering The M. S. University of Baroda Vadodara- 390 001 Gujarat, India

February 2014

#### Tel: 2434188 extn.415, 212



#### APPLIED CHEMISTRY DEPARTMENT

Faculty of Technology & Engineering The Maharaja Sayajirao University of Baroda Post Box No: 51, Kalabhavan Vadodara- 390 001 (India)

DST-FIST Sponsored Department

Ref. No. App Ch./Date: 10/02/2014

### **CERTIFICATE**

This is to certify that the thesis entitled "Synthesis and characterization of watersoluble low molecular weight polymers" submitted by Ms. Renu Singh to The M. S. University of Baroda, Vadodara for the award of Ph.D. degree in Applied Chemistry incorporates the original research work carried out by her under my supervision.

Prof. C. N. Murthy **Research Guide Applied Chemistry Department** 

Head **Applied Chemistry Department** 

Dean Faculty of Technology & Engineering The M. S. University of Baroda

#### DECLARATION

I state that the work presented in this thesis entitled "**Synthesis and characterization** of water-soluble low molecular weight polymers" comprises independent investigations carried out by me under the guidance of Prof. C. N. Murthy. Wherever references have been made to the work of others, it has been clearly indicated with the source of information under the references section. The matter presented in this thesis has not been submitted elsewhere for the award of any other degree.

Signature of the Candidate

(Renu Singh)

#### Acknowledgements

I would like to take this opportunity to thank my supervisor, Prof. C. N. Murthy, for his invaluable guidance, encouragement and support in the period of this study and preparation of the thesis. His constructive suggestions helped me to come through all the difficulties during my research work. It was my privilege to work under his able guidance. I consider it a great opportunity to have been his student, and I will ever remain grateful to him.

This work would not have been possible without financial support. I thank UGC for providing me financial support under the RFSMS scheme.

I am deeply thankful to Prof. P. T. Deota, Head, Applied Chemistry Department, for his continual support and encouragement during my research work. I also like to thank Prof. D. P. Bharambe for his support in hostel accommodation and for moral support also. I gratefully express my deep appreciation to Dr. Indrajit Shown, Dr. Santosh Kumar, Dr. R. Murali, and Dr. Vinod I. Bhoi, for invaluable help by providing their guidance and sharing experiences during the peak of my experimental work.

I would like to thank my fellow research colleagues Dr. Parimal Patel, Dr. Mayur Patel, Gautam Patel, Vaishali Suthar, Umesh Chaudhari, Gangadhar Tamanna, Prachi Shah, Dr. Shweta Gupta, Brijesh Shah, Srinivas Ghodke, Tarun Parangi, Pavan Karkare, and Pranav Chitte for their encouragement during my research work.

I also cordially like to thank my hostel group Dr. Kavita Yadav, Poulami Paria, Meenu Singh, Somila Surbhi, Rooby, Krupa, Mansi, Vibha, Parimala Desai, Ankita Viradiya, Minal and Rasika.

I am thankful to all the teaching and non-teaching staff of the Applied Chemistry Department for supporting me throughout my research work.

My deepest heartfelt gratitude to my brothers & sister-in-laws for their moral support and making me pass through the difficult situations with great ease during my prolonged years of research work. More importantly, I would like to deeply acknowledge my parents for their invaluable support and blessings throughout my study. Without their support, I could not be able to complete this study.

**Renu Singh** 

I dedicate this thesis to my parents

# B. P. SINGH

Ŀ

# RAJKESARI DEVI

# AND

# MY BROTHERS

for their support, patience & blessings

## **TABLE OF CONTENTS**

List of Figu	ires	IX-XI
List of Sche	emes	XII
List of Tab	les	XIII
Abbreviatio	ons	XIV
Chapter 1		1-33
	Introduction	
1.1	Water-Soluble Polymers	1
1.1.1	Synthetic water-soluble Polymers	2
	1.1.1.1.Polyacrylic acid (PAA)	3
1.1.2	Natural Water-Soluble Polymers	9
1.1.2.1	Chitosan Derivatives	
1.1.2.1.1	Chitosan derivatives of importance	11
	1.1.2.1.1.1 Quaternized chitosan and N-alkyl chitosan	12
	1.1.2.1.1.2 Highly cationic derivatives	12
	1.1.2.1.1.3 Hydroxyalkyl chitosans	13
	1.1.2.1.1.4 Carboxyalkyl chitosans	13
	1.1.2.1.1.5 Sugar-modified chitosan	14
	1.1.2.1.1.6 Cyclodextrin linked chitosan	15
	1.1.2.1.1.7 N-Acyl chitosan	16
	1.1.2.1.1.8 O-Acyl chitosan	17
	1.1.2.1.1.9 Thiolated chitosan	18
	1.1.2.1.1.10 Sulfated chitosan	20
1.1.2.1.2	Enzymatic modification of chitosan	21
1.1.2.1.3	Graft copolymers of chitosan	22
1.1.2.1.4	Chitosan-dendrimer hybrid	22
1.1.2.1.5	Cyclic-host bound chitosan	23
1.2	References	25

	of poly (acrylic acid)	
2.1	Introduction	34
2.2	Experimental	38
	2.2.1 Materials	38
	2.2.2 Instruments and Measurements	38
	2.2.3 Synthesis	38
	(A) Synthesis of PAA by varying concentration of initiators	38
	(B) Synthesis of PAA by varying concentration of inhibitors	40
	2.2.4 Determination of metallic sequestration capability of	41
	PAAs	
2.3	Results and Discussion	42
	2.3.1 FT-IR Spectra	42
	2.3.2 Viscosity average method	43
	(A) Viscosity plot for PAA samples from variation in	44
	concentration of initiator	
	(B) Viscosity plot for PAA samples from variation in	54
	concentration of inhibitors (i.e., Allyl alcohol &	
	Allyl chloride)	
	2.3.3 Metallic Sequestration Capability Study	60
2.4	Conclusions	63
2.5	References	64
Chapter 3	Synthesis of Hydrogels from template polymerization of	67-90
	acrylic acid on to modified chitosan	
3.1	Introduction	67
3.2	Experimental	71
	3.1.1 Materials	71
	3.2.2 Instruments and Measurements	71
	3.2.3 Synthesis of 6-amino-6-deoxy-chitosan	71

## Chapter 2 Effect of initiator and inhibitor on the molecular weight 34-66 of poly (acrylic acid)

	3.2.4 Graft copolymerization of acrylic acid on 6-amino-6-	74
	deoxy-chitosan	
3.3	Results and Discussion	76
	3.3.1 FT-IR spectra	76
	3.3.2 Thermal Analysis (TGA)	79
	3.3.3 Measurement of water absorbancy	81
	3.3.4 Swelling behavior	83
	3.3.5 SEM & EDX analysis	85
3.4	Conclusions	88
3.5	References	89
	Summary of the Work	91
	List of Publications	93
	List of Presentations	93

## List of Figures

Figure	Title	Page No
1.1	Different Functions/Applications of Water-soluble Polymers	1
1.2	World Consumption of Water-soluble Polymers	2
1.3	Schematic illustration of chitosan's solubility in different medium	5
1.4	Chemical structure of chitin, chitosan and 6-amino-6-	10
	chitosan	
1.5	Amenable functional groups in chitosan.	12
1.6	Example of sugar-modified Chitosan	17
1.7	Example of cyclodextrin linked chitosan	19
1.8	Synthesis of acyl Chitosan	21
1.9	Synthesis of thiolated Chitosan	22
1.10	Example of sulfated Chitosan	24
1.11	Example of cyclic host bound chitosan	25
2.1	A schematic outline depicting the various phases of scale	36
	formation	
2.2	FT-IR spectra of PAA	42
2.3	Ubbelohde Viscometer	43
2.4	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	44
	for PAA-I	
2.5	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	45
	for PAA-II	
2.6	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	46
	for PAA-III	
2.7	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	47
	for PAA-IV	
2.8	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	48
	for PAA-V	
2.9	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	49

	for PAA-VI	
2.10	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	50
	for PAA-VII	
2.11	Plot for viscosity data for computing intrinsic viscosity $[\boldsymbol{\eta}]$	51
	for PAA-VIII	
2.12	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	52
	for PAA-IX	
2.13	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	53
	for PAA-X	
2.14	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	54
	for PAA-XI	
2.15	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	55
	for PAA-XII	
2.16	Plot for viscosity data for computing intrinsic viscosity [η]	56
	for PAA-XIII	
2.17	Plot for viscosity data for computing intrinsic viscosity [ŋ]	57
	for PAA-XIV	
2.18	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	58
	for PAA-XV	
2.19	Plot for viscosity data for computing intrinsic viscosity $[\eta]$	59
2 20	for PAA-XVI	60
2.20	Schematic representation of metallic sequestration through	60
0.01	PAA	<i>c</i> 1
2.21	Graphical representation of relation between molecular	61
	weight & metallic sequestration	
2.22	Graphical representation of relation between molecular	62
	weight & metallic sequestration	
3.1	Schematic illustration of the transit of superporous hydrogel	67
3.2	Brief introductions of chitin & chitosan	69
3.3	FT-IR spectra of (a) Chitosan to 6a6dC and (b) 6a6dC, PAA	77
	& 6a6dC-g-PAA	
3.4	TGA of chitosan, 6a6dC and 6a6dC-g-PAA	80
3.5	Water uptake (%) capacity of 6a6dC-g-PAA	82

3.6	Water absorption capacity at different pH range	84
3.7	SEM analysis of (a) Chitosan, (b) C-g-PAA, (c) 6a6dC & (d) 6a6dC-g-PAA	85
3.8	EDX analysis of (a) Chitosan & (b) 6-amino-6- deoxychitosan	86

### List of Schemes

Scheme No	Title	Page No
2.1	Synthesis of poly(acrylic acid) with mechanism	39
2.2	Synthesis of poly (acrylic acid) by using inhibitor with mechanism	41
3.1	Preparation of 6-amino-6-deoxy-chitosan	73
3.2	Graft copolymerization of 6-amino-6-deoxy-chitosan with acrylic acid	75

### List of Tables

Table No	Title	Page No
2.1	Viscosity data for a PAA-I in 1, 4-dioxane solution at RT	44
2.2	Viscosity data for a PAA-II in 1, 4-dioxane solution at RT	45
2.3	Viscosity data for a PAA-III in 1, 4-dioxane solution at RT	46
2.4	Viscosity data for a PAA-IV in 1, 4-dioxane solution at RT	47
2.5	Viscosity data for a PAA-V in 1, 4-dioxane solution at RT	48
2.6	Viscosity data for a PAA-VI in 1, 4-dioxane solution at RT	49
2.7	Viscosity data for a PAA-VII in 1, 4-dioxane solution at RT	50
2.8	Viscosity data for a PAA-VIII in 1, 4-dioxane solution at RT	51
2.9	Viscosity data for a PAA-IX in 1, 4-dioxane solution at RT	52
2.10	Viscosity data for a PAA-X in 1, 4-dioxane solution at RT	53
2.11	Viscosity data for a PAA-XI in 1, 4-dioxane solution at RT	54
2.12	Viscosity data for a PAA-XII in 1, 4-dioxane solution at RT	55
2.13	Viscosity data for a PAA-XIII in 1, 4-dioxane solution at RT	56
2.14	Viscosity data for a PAA-XIV in 1, 4-dioxane solution at RT	57
2.15	Viscosity data for a PAA-XV in 1, 4-dioxane solution at RT	58
2.16	Viscosity data for a PAA-XVI in 1, 4-dioxane solution at RT	59
2.17	Composition of reactants with sequestration value &	61
	Molecular weight of PAAs	
2.18	For Allyl Alcohol: Composition of reactants with	62
2 10	sequestration value & Molecular weight of PAAs	62
2.19	For Allyl Chloride: Composition of reactants with sequestration value & Molecular weight of PAAs	02
	sequestiation value & molecular weight of 1 AAs	

### Abbreviations

WSP	Water Soluble Polymer
LMW	Low Molecular Weight
HMW	High Molecular Weight
$M_n$	Number Average Molecular Weight
DP	degree of polymerization
PAA	Poly(acrylic acid)
CS	Chitosan
6A6DC	6-amino-6-deoxychitosan
AR	Analytical Reagent
RM	Room Temperature
EtOH	Ethyl Alcohol
EDX	Electron Dispersive X-ray Spectroscopy
EDX TPP	Electron Dispersive X-ray Spectroscopy Triphenyl phosphine
TPP	Triphenyl phosphine
TPP TsCl	Triphenyl phosphine p-Toluene sulfonyl chloride
TPP TsCl ppm	Triphenyl phosphine p-Toluene sulfonyl chloride Parts Per Million
TPP TsCl ppm MWCO	Triphenyl phosphine p-Toluene sulfonyl chloride Parts Per Million Molecular Weight Cut-Off
TPP TsCl ppm MWCO FTIR	Triphenyl phosphine p-Toluene sulfonyl chloride Parts Per Million Molecular Weight Cut-Off Fourier Transform Infrared
TPP TsCl ppm MWCO FTIR TGA	Triphenyl phosphine p-Toluene sulfonyl chloride Parts Per Million Molecular Weight Cut-Off Fourier Transform Infrared Thermal Gravimetric Analysis