ICROSTRUCTURE DETERMINATION OF VINYL TERPOLYMERS BY ONE AND TWO DIMENSIONAL NMR SPECTROSCOPY

by

N.M. SHAHRYAR KHAN HEKMATYAR
DEPARTMENT OF CHEMISTRY

Submitted
in fulfillment of the requirements of the degree of
DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI
INDIA
FEBRUARY, 2000

Dedicated

WITH LOVE,
TO MY APPA

/HO COULD NOT SEE ME HERE

Vinyl polymers;
NMR spectroscopy

CERTIFICATE

This is to certify that the thesis entitled, "**MICROSTRUCTURE DETERMINATION OF VINYL TERPOLYMERS BY ONE AND TWO DIMENSIONAL NMR SPECTROSCOPY**", being submitted by **Mr. N.M. Shahryar Khan Hekmatyar** to Indian Institute of Technology, Delhi for the award of Degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. Mr. N.M. Shahryar Khan Hekmatyar has worked under my supervision and guidance and has fulfilled all the requirements for the submission of this thesis which to my knowledge has reached the requisite standard.

The work embodied in this thesis has not been submitted, in part or full to any other University or Institute for the award of any degree or diploma.

(A.S.Brar)
Thesis Supervisor
Professor
Department of Chemistry
Indian Institute of Technology
New Delhi-110016
India.

ACKNOWLEDGEMENTS

Words are wholly inadequate to express my appreciation to those people whose love, guidance, endurance and constant inspiration helped me in making of this thesis.

I wish to thank my **Prof. A.S. Brar** who implanted in me the concept of NMR from date of joining to the end with constant inquiry and goading and allowed me to my first venture into the wonderful world of NMR and structure determination. He who spent years in working with me, spending so much of his time to flood me with the ideas for the writing of this thesis. I am again particularly grateful to **Prof. A.S.Brar** for a most careful, critical reading and for saving me from a number of pitfalls.

I will be failing in my duty if I do not thank **Prof. M. N. Gupta, The Head, Prof. R. C. Anand, Dr. Ravishankar, Dr. B. Jayaram** and **Dr. N. D. Kurur** and **Dr. A. Ramanan** since I interacted with them with benefit and benevolance for invaluable suggestions.

I would like to thank the people at NMR lab **Mr. Bala Dutt, Mr. Munna Lal** and **Mr. Keshav,** whose dedication and flexibility went long way in the completion of this thesis. It was a matter of great pleasure in working with all these competent professionals.

Thanks are due to **Mr.Aggarwal, Mr.R.K.Singh and Mrs. Shanta** for assisting me during my work in the instrumentation lab and **Mr. Prasad** and **Mr. Gupta** for preparing and scanning several spectra for my thesis.

I am grateful to **Department of Science and Technology, CSIR, New Delhi** and **IIT. Delhi** for financial supports and facilities.

I have been immensely from the advice, criticism and encouragement of several my colleagues. To mention a few are **Rajeev, Pradhan, Anubav, Anil, Thiagu, Dr. Meenashki, Dr. Munia and Dr. Kaushik.**

My greatest debt is to the many friends in my batch *Thonti* **Durai,** *Kurukku kanakku* **Dr. Patrick,** *Aruvai* **Dr.Ayyappan, Sooriya,** *Kallapatti* **Charles,** *Seashore*

Samy, Senior friends *Rakkoli* **Rajagopal, Thirumal, Dr.Amburose,** in my hostel *Yakoob* **John,** *Thesaka* **Venkatesh,** *Slater* **Srinivas,** *Paalsamy* **Bala** and around globe *Mac* **Krishna** and **Guru,** who have with their own hectic work and their inspiration and day to day cooperation over so many years provided new incentive for my continued activity in research.

My heartfelt thanks to *late* **my Appa,** I am deeply appreciation of his patience and buoyance and have pleasure to dedicate this thesis to him.

There have been many people who contributed through ideas, support and suggestions, I really appreciate their efforts. But one whose affection, tolerance and sacrifice through out my life are **my parent and my uncle,** without their everlasting love, moral support and understanding, the whole work could not have been accomplished.

Last but not least, I thank **Allah** for showing me the right path, giving me the right spirit and health during my life.

Shahryar Khan Hekmatyar

ABSTRACT

Research on polymers has been mainly addressed to the synthesis of new materials with specific performance for the last 30 years. A wide variety of chemical or physical strategies including copolymerization, polymer blends and composities or crosslinking network have been explored to match the individual requirements. Terpolymerization have continued to evoke interest from both academics and industrialists. One of the main advantages of this terpolymerization technique is that it provides a convenient method of synthesizing new polymeric structures with wide range of properties. Although extensive literature is available for the homopolymerization and copolymerization, very little kinetic or synthetic and structural information is available for the terpolymerization. As it becomes more and more possible to "tailor-make" polymers with specific physical and chemical properties, it will undoubtedly become necessary to resort to such multiple combinations, wherein each monomer contributes some particular property or properties.

for example

(a) a copolymer into which a small amount of third monomer is introduced for the purpose of providing functional groups for subsequent crosslinking reactions.

(b) a copolymer with desirable solubility and mechanical properties into which a certain amount of a polar monomer is introduced in order to improve its adhesive properties.

So, the interest in the multifunctional synthetic polymers or copolymers is steadily increasing as macromolecular catalyst, macromolecular drugs or anti-static agents.

The growth in the production of plastic materials during the past few years has been accompanied by an increased demand for the materials with improved physical and mechanical properties, greater heat and radiation stability etc. Only a few homopolymers and copolymers can satisfy such demands.

The physical and the chemical properties are proved to be influenced fundamentally by the microstructure of these polymers, which involves the characterization of monomer sequence distribution in the polymer chain and the stereochemical and compositional arrangements of various monomer units in the polymer. The information concerning the microstructure of a polymer is also essential for clarifying the polymerisation mechanism.

NMR technique has been proven to be the most powerful experimental tool for investigating the microstructure of vinyl homo and copolymers. This is due to the fact the NMR chemical shifts are sensitive to the chemical and stereochemical structure of the different units constituting the polymer chain.

Keeping in view with the significance of the polymer microstructure, a work was undertaken with a purpose to develop the theoretical and experimental basis for analysing the structure of vinyl terpolymer chains at molecular level. The stereochemical and compositional structure of homopolymers and copolymers were investigated by means of combination of one and two dimensional NMR spectroscopy. Traditional techniques (one dimensional experiments) were not always suitable for unequivocal signal assignments. The 2D NMR techniques especially homonuclear correlated spectroscopy (COSY) and heteronuclear shift quantum correlation spectroscopy (HSQC) have been applied in determining the stereochemical and compositional sequences of number of polymer systems. In this research work, we have

tried to determine the compositional and configurational sequences of vinyl terpolymers using one dimensional (^1H, $^{13}C\{^1H\}$ NMR and DEPT) and two dimensional (DQF COSY, TOCSY, inverse-HETCOR and NOESY) experiments.

The thesis consists of eight chapters. The first chapter describes the general introduction about the microstructure and the review of the literature. It also describes the use of two dimensional NMR spectroscopy for sequence determination.

The second chapter describes the experimental procedures for the preparation of homopolymers, copolymers and terpolymers. Experimental details of the molecular weight determined by GPC is also given. The composition of the copolymers and terpolymers were determined from ^1H, quantitative $^{13}C\{^1H\}$ NMR and nitrogen analysis. This chapter also gives the detailed description of all the one and two dimensional NMR experiments carried out for the investigation of this research work. It discusses about the theoretical sequence distribution by Harwood, Monte Carlo simulations and TERSEQ program.

The third chapter deals with the sequence determination of the acrylonitrile/styrene (A/S), acrylonitrile/methyl methacrylate(A/M) and styrene/methyl methacrylate (S/M) copolymers. The copolymers of (A/S), (A/M) and (S/M) were prepared by photopolymerization using uranyl ion as a photosensitizer. The composition of the copolymer was determined from the ^1H NMR, quantitative $^{13}C\{^1H\}$ NMR and the nitrogen content in the copolymers. The comonomer reactivity ratios were determined by both Kelen Tudos (KT) and non-linear error in variables (EVM) methods using the copolymer composition data. The reactivity ratios calculated for the A/S copolymers are $r_A = 0.03$ and $r_S = 0.33$; for A/M copolymers are $r_A = 0.17$ and $r_M = 1.45$; and for the (S/M) copolymers $r_S = 0.52$ and $r_M = 0.47$. The microstructure was obtained in terms of

the distribution of A-, S- and M-centered triad sequences from $^{13}C\{^1H\}$-NMR spectra of the copolymers. Heteronuclear 2D HSQC NMR were used to simplify the complex ^1H NMR spectra of the copolymer. The 2D TOCSY experiments were used to make unambiguous assignments from the various coupling between the protons of the copolymers. 2D NOESY spectrum was employed to find out the various spatial coupling between the protons. There is good agreement between the experimentally obtained (NMR) triad fractions, those calculated from theoretical models and MC simulations. The triad concentrations determined from NMR using the carbonyl, quaternary and nitrile carbon resonances, were found out to follow first order Markov model.

The microstructure of the acrylonitrile/styrene/methyl methacrylate terpolymers have been in chapter IV. These terpolymers were prepared by photopolymerization using uranyl ion as photosensitizer. The composition of the terpolymers were calculated by Goldfinger's equation using comonomer reactivity ratios $r_A = 0.03$ and $r_S = 0.33$; $r_A = 0.17$ and $r_M = 1.45$; $r_S = 0.52$, $r_M = 0.47$. The sequence assignments obtained from $^{13}C\{^1H\}$ NMR spectra of the terpolymer were in good agreement with triad concentrations calculated from the statistical model. The complete spectral assignment of the overlapping proton and carbon spectra of these terpolymers were done with the help of Distortionless Enhancement by Polarization Transfer (DEPT) and two dimensional ^1H-^{13}C heteronuclear shift quantum correlation (HSQC) and homonuclear total correlation spectroscopy (TOCSY) experiments. 2D Double Quantum Filtered phase sensitive homonuclear shift correlation (DQF-COSY) spectroscopy was used to ascertain the various geminal couplings between the methylene protons.

The fifth chapter deals with the microstructure determination of the

acrylonitrile/methyl acrylate and methyl acrylate/styrene copolymers. The methine, methylene, carbonyl, nitrile and quaternary carbon resonances were assigned to triad, tetrad and pentad sequences respectively. The triad concentrations were calculated using the carbonyl, quaternary and nitrile carbon resonances. The various configurational assignments in the aliphatic region of the copolymers were done with the help of HETCOR, homonuclear COSY and TOCSY experiments. The reactivity ratios of these copolymers are $r_A = 1.03$ and $r_M = 0.74$; $r_S = 1.16$ and $r_M = 0.19$; determined from KT and EVM methods using the copolymer composition data, which were obtained from the ^1H NMR and CHN analysis of the copolymers. Monte Carlo simulation was used to study the effect of the degree of polymerization on the triad fractions.

The sixth chapter is devoted to the terpolymers of acrylonitrile-styrene-methyl acrylate and its terpolymerization composition was determined using the reactivity ratios $r_A = 0.03$ and $r_S = 0.33$; $r_A = 1.03$ and $r_M = 0.74$; $r_S = 1.16$ and $r_M = 0.19$; from the $^{13}C\{^1H\}$ quantitative NMR. The triad fraction values for various A- , S- and M- centered triad were calculated using the comonomer reactivity ratios. The terpolymer mechanism was determined using the triad concentrations calculated from the nitrile, quaternary and carbonyl carbon resonance signals from the $^{13}C\{^1H\}$ NMR. The various carbon resonance signals were assigned with the help of DEPT NMR.

The chapter VII illustrates the third type of the copolymer systems, styrene-methacrylic acid (S/M), methacrylic acid-vinylidene chloride (M/V) and styrene-vinylidene chloride (S/V). The preparation, copolymer composition determination, triad calculation using various M-, S- and V- centered triads were discussed in this Chapter. Monte Carlo simulation were also used for determining the triad fraction and for studying the variation of S-, M- and V- centered triads as a function of fractional

conversion. The reactivity ratios calculated for the three types of the copolymers were r_S = 0.14 and r_M = 0.61; r_S =1.39 and r_V =0.13; r_M=2.41 and r_V =0.09; respectively. The methylene and methine carbon resonance signals were analysed with the help of DEPT and HETCOR NMR spectroscopy. 2D TOCSY and NOESY experiments were employed to assign the various through bond and spatial couplings.

The Chapter VIII discusses sequencing of styrene/ vinylidene chloride/ methacrylic acid terpolymer were prepared by the photo polymerization and its composition was calculated with the help of $^{13}C\{^1H\}$ NMR spectroscopy using the comonomer reactivity ratios r_S = 0.14 and r_M = 0.61; r_S =1.39 and r_V =0.13; r_M=2.41 and r_V =0.09 respectively. It was compared with values calculated from the Goldfinger's equation. DEPT and HSQC NMR were employed to differentiate the overlapping resonance sequences of the terpolymer. 2D NOESY was used to find out various spatial couplings.

CONTENTS

Certificate		(i)
Acknowledgement		(ii)
Abstract		(iv)
		Page. No.
CHAPTER I	**INTRODUCTION**	
1.1	Introduction	1
1.2	NMR Spectroscopy	3
1.3	NMR of Homopolymers	3
1.4	NMR of Copolymers	6
1.5	NMR of Terpolymers	8
1.6	Copolymerization Models	9
	1.6.1(a)The Terminal Model	9
	1.6.1(b)Ternary Copolymerization	11
1.7	Monte Carlo Simulation	12
1.8	Reactivity Ratio Determinations	13
	References	14
CHAPTER II		
2.1	Purification of Monomers	22
2.2	Preparation of Homopolymers	22
2.3	Preparation of Copolymers and Terpolymers	22
2.4	Molecular Weight Determination	22

2.5		NMR Analysis	23
2.6		Theoretical Sequence Determination	25
2.7		Monte Carlo Simulations	25
2.8		Reactivity Ratio Determination	25
2.9		Elemental Analysis	26
		References	26

CHAPTER III: ACRYLONITRILE/STYRENE, ACRYLONITRILE/ METHYL METHACRYLATE AND STYRENE/ METHYL METHACRYLATE COPOLYMERS

3.1		Introduction	27
3.2		Acrylonitrile/Styrene Copolymers	31
	3.2.1	Reactivity Ratio Determination	31
	3.2.2	^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies	33
	3.2.3	2D NMR Studies	42
	3.2.4	Monte Carlo Simulation Studies	46
3.3		Acrylonitrile/Methyl methacrylate Copolymers	48
	3.3.1	Reactivity Ratio Determination	48
	3.3.2	^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies	48
	3.3.3	2D NMR Studies	63
	3.3.4	Monte Carlo Simulation Studies	68
3.4		Styrene/Methyl methacrylate Copolymers	70
	3.4.1	Reactivity Ratio Determination	70
	3.4.2	^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies	70
	3.4.3	2D NMR Studies	76
	3.4.4	Monte Carlo Simulation Studies	83

3.5		Conclusions	85
		References	86

CHAPTER IV: ACRYLONITRILE/ STYRENE/ METHYL METHACRYLATE TERPOLYMERS

4.1		Introduction	89
4.2		Acrylonitrile/Styrene/ Methyl methacrylate Terpolymers	91
	4.2.1	Compositions Determination	91
	4.2.2	^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies	91
	4.2.3	2D NMR Studies	104
4.3		Conclusions	111
		References	111

CHAPTER V: ACRYLONITRILE/METHYL ACRYLATE AND METHYL ACRYLATE /STYRENE COPOLYMERS

5.1		Introduction	113
5.2		Acrylonitrile/Methyl acrylate Copolymers	117
	5.2.1	Reactivity Ratio Determination	117
	5.2.2	^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies	117
	5.2.3	2D NMR Studies	123
	5.2.4	Monte Carlo Simulation Studies	129
5.3		Methyl acrylate/Styrene Copolymers	129
	5.3.1	Reactivity Ratio Determination	129
	5.3.2	^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies	131
	5.3.3	2D NMR Studies	136
	5.3.4	Monte Carlo Simulation Studies	140

5.4 Conclusions 142

References 142

CHAPTER VI: ACRYLONITRILE/ STYRENE/ METHYL ACRYLATE TERPOLYMERS

6.1 Introduction 145

6.2 Acrylonitrile/Styrene/Methyl acrylate Terpolymers 147

6.2.1 Compositions Determination 147

6.2.2 ^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies 147

6.2.3 2D NMR Studies 160

6.3 Conclusions 165

References 165

CHAPTER VII: STYRENE/VINYLIDENE CHLORIDE, METHACRYLIC ACID/ VINYLIDENE CHLORIDE AND STYRENE/ METHACRYLIC ACID COPOLYMERS

7.1 Introduction 167

7.2 Styrene/Vinylidene Chloride Copolymers 171

7.2.1 Reactivity Ratio Determination 171

7.2.2 ^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies 171

7.2.3 2D NMR Studies 175

7.2.4 Monte Carlo Simulation Studies 182

7.3 Methacrylic acid/Vinylidene Chloride Copolymers 184

7.3.1 Reactivity Ratio Determination 184

	7.3.2	^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies	186
	7.3.3	2D NMR Studies	193
	7.3.4	Monte Carlo Simulation Studies	200
7.4		Styrene/Methacrylic acid Copolymers	202
	7.4.1	Reactivity Ratio Determination	202
	7.4.2	^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies	203
	7.4.3	2D NMR Studies	210
	7.4.4	Monte Carlo Simulation Studies	217
7.5		Conclusions	217
		References	218

CHAPTER VIII: STYRENE/VINYLIDENE CHLORIDE/ METHACRYLIC ACID TERPOLYMERS

8.1		Introduction	221
8.2		Styrene/Vinylidene chloride/ Methacrylic acid Terpolymers	222
	8.2.1	Compositions Determination	222
	8.2.2	^{1}H & ^{13}C $\{^{1}H\}$ NMR Studies	223
	8.2.3	2D NMR Studies	234
8.3		Conclusions	240
		References	240
		Resume	242