

**NMR STUDIES OF VINYL POLYMERS
SYNTHESIZED BY ATOM TRANSFER RADICAL
POLYMERIZATION**

by

SUKHDEEP KAUR

DEPARTMENT OF CHEMISTRY

Submitted

in fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the

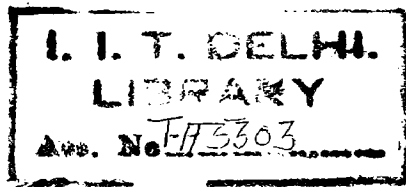


INDIAN INSTITUTE OF TECHNOLOGY, DELHI

MARCH, 2006

Macromolecules
Polymers for auto
6

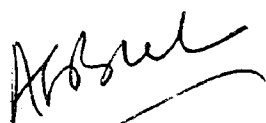
TH
541.64
SUK-N



Certificate

This is to certify that the thesis entitled, "NMR STUDIES OF VINYL POLYMERS SYNTHESIZED BY ATOM TRANSFER RADICAL POLYMERIZATION", being submitted by Mrs. Sukhdeep Kaur to Indian Institute of Technology, Delhi, for the award of the Degree of Doctor of Philosophy, is a record of bonafied research work carried out by her. Mrs. Sukhdeep Kaur has worked under my supervision and guidance and has fulfilled all the requirements for the submission of a Ph.D. thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of the Ph.D. degree.

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,
Delhi
Hauz Khas
New Delhi – 110016
INDIA

Dedicated
To

His Holiness
Shri Satguru Jagjit Singh Ji

Acknowledgments

The transformation of my research work into the thesis form is all because of the blessings of the Almighty, H. H. Satguru Jagjit Singh Ji. The presence of His blessings protected me in every sense and gave me motivation to go on even when it seemed that the research road was becoming directionless. The resurgence and perserverence which He gave me in one way or the other has turned me into a more mature and responsible person.

Prof. A. S. Brar, my research advisor, is a person who has always been a source of inspiration to me. In my initial period of research, he was very busy with the administration work but he had always time to listen and discuss the data and problems. He is a person who will always be there for you whenever or whatever.

I wish to thank Prof. H. M. Chawla and Prof. U. K. Nadir (Head of Department) for providing all the facilities and access to the instrumentation.

I wish to thank Mr. Munna Lal and Mr. R. K. Singh, lab technicians in NMR lab, Mr. Agarwal, Mrs. Shanta, Mr. Sharma and Mr. Kuldip of Instrumentation lab and Mr. Sehgal and Mr. Singh of Stores.

I wish to thank Dr. Pradhan, Dr Anil and Dr Manpreet, my seniors for sharing their knowledge and experiences in research work and NMR.

Gurmeet, Me, Meghna, Tripta and Sonia, are the ones who have really enjoyed our tenure as research scholars to the fullest. This research period has seen me grow from a girl to a wife and finally a mother.

Gurmeet, my class fellow, senior (lab) and now my dear husband, is the one to whom I have always looked upon as ray of hope and direction no matter what type of time we are going through. He is one responsible for turning an immature, asinine girl into a confident and complete lady. He is one who is behind all the best publications I had during my research. I don't know how, but he managed to scoop out the best in me and show me how to live life fully. Gurmeet, thanks for coming into my life.

Meghna, unique and rarest of gem in my life, somebody more than a friend and person one always wishes to have in life. She is one who just pushed me into organic synthesis just on her confidence in me. She has touched my life in many ways and many aspects. I have no words to express my feelings for her. I just wish that we always remain like that forever.


Joining of Tripta as research scholar in our lab was the best thing that could have happened. She is a very sweet person with lots of affection and warmth, making sure that people around her feel comfortable by her presence. We have seen each other grow from the time of M. Sc. at IIT-Delhi. She holds a special place in my life for she has given me so many things to cherish and feel happy.

Sonia, the only junior in lab, a chirpy little girl full of fun and frolic, has made a mark in my life. She is a loving girl and I wish all the best things for her in life.

I wish to thank Dr. Naveen whose one push pulled me out from the problem which I got struck during my synthesis work. I also wish to thank Jaspreet for her support.

I wish to thank my parents for their constant support, inspiration and adjustments which they have made during my tenureship. Their sacrifices and strengths made me sail off smoothly during hard times. I also wish to thank my sisters, Gagandeep and Meetraman for their encouragement.

Finally, I wish to thank my father-in-law and mother-in-law for their care, affection and endorsement. Their unconditional love and constant support has made my head bow with respect for them. I wish a blissful and healthy life for them from the Almighty. I also pray that I always remain under their showers of blessings. I am really lucky to have such affectionate in laws around me who have always made my life comfortable.


(Sukhdeep Kaur)

Abstract

Atom Transfer Radical Polymerization (ATRP) is one of the versatile techniques of Controlled Radical Polymerization (CRP) which gives finer control over molecular weight and polymer architecture. Besides having the advantages of Free Radical Polymerization (FRP) i.e. tolerance towards functional groups and impurities, ATRP involves uniform growth of polymer chain throughout the polymerization hence eliminating termination reaction and side reactions like chain transfer etc to minimum extend.

ATRP was reported simultaneously by Matyjaszewski et al. and Sawamoto et al. in 1995. Its initially application was on the synthesis of homopolymers having targeted molecular weights with low polydispersity. Gradually, ATRP was being used as a successful technique for preparation of copolymers like random, gradient, block, triblock, star etc. In recent years, ATRP has been successfully employed for the polymerization of various other monomers beside the standard ones. ATRP provides the choice to prepare polymers of desired molecular weight as well as structure, composition and architecture.

NMR plays a poignant role in monitoring extends of reaction, checking the purity of polymer sample along with its identification and establishing polymer microstructure. The combination of newer 2D NMR techniques with the 1D NMR experiments helping determining and detection of end group functionality and tacticity.

The thesis consists of six chapters. The work done in the field “Atom Transfer Radical Polymerization” and “NMR of Polymers” has been surveyed and its impact on the current status of research being undertaken in the polymer

chemistry has been reviewed in *Chapter 1*. The chapter signifies the importance of the research project undertaken in the field of polymer chemistry. A general introduction to ATRP, with special emphasis on the mechanism, kinetics and importance of the various components involved in the mechanism is covered. Role of NMR in ATRP has been evaluated in this chapter.

Chapter 2 contains the experimental details of synthesis of new ligand i.e. Tetramethylguanidino-tris(2-aminoethyl)amine (TMG₃-TREN) for copper based ATRP and also the synthesis of tris(2-(dimethylamino)ethyl)amine (Me₆-TREN). The details for synthesis of new initiator, N-2-bromoethyl carbazole (NBC) for homopolymerization of N-vinyl carbazole by ATRP and optimization of reaction conditions is also provided. The experimental details for the optimization and standardization of homopolymerizations, copolymerizations and block reactions through ATRP using well known catalysts are reported.

In the characterization of polymers synthesized, determination of molecular weight and molecular weight distribution by Gel Permeation Chromatography is provided. The experimental details for the 1D ¹H, ¹³C{¹H}, DEPT-45, 90 and 135; 2D Heteronuclear Single Quantum Correlation (HSQC), Total Correlation Spectroscopy (TOCSY) and Heteronuclear Multi Bond Correlation (HMBC) NMR experiments are incorporated. The theoretical basis and the experimental details about the optimization of the reactivity ratios from the infeed/outfeed fractions using the least square methodology are also given.

Chapter 3 deals with the evaluation of catalytic performance of a tripod amine ligand i.e. Tetramethylguanidino-tris(2-aminoethyl)amine (TMG₃-TREN) for copper based ATRP for standard monomers like methyl methacrylate, n-butyl

acrylate, styrene and acrylonitrile. Our aim regarding the study of this catalyst was to obtain polymers having low polydispersity, predictable molecular weights and most of all, good control of polymerizations with reduced amount of catalyst. A comparative study of the performance of this catalyst with the already established catalyst CuBr/ Me₆-TREN was also done.

The homopolymer poly(methyl methacrylate) (PMMA) synthesized using the catalyst CuBr/TMG₃-TREN was well-defined both in bulk and solution. Comparing the performance of ATRP using Me₆-TREN copper complex with CuBr/TMG₃-TREN, MMA polymerization was more feasible and easy to perform with the latter copper complex.

While the polymerization conducted using TMG₃-TREN as ligand for n-butyl acrylate behaved in the similar pattern as for CuBr/Me₆-TREN in terms of catalyst concentration and monomer conversion, the main demarcation was that all polymerizations using TMG₃-TREN occurred at ambient temperature and at relatively faster rate.

The polymerization of styrene using CuBr/TMG₃-TREN was not well controlled and the curvature observed indicated that termination was not negligible. In comparison of these results with those for the same system with Me₆-TREN as the ligand, the system with Me₆-TREN showed better controllability and were much faster.

Well-defined polyacrylonitrile (PAN) has been successfully synthesized only by CuBr/2,2'-bipyridine catalyst. On comparing the results with those published for the AN polymerization with 2,2'-bipyridine, performance of TMG₃-

TREN as a ligand for copper based ATRP was on the similar lines with advantage of faster polymerization without affecting the molecular weight distribution.

^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR substantiated the presence of end groups. The isotactic parameters calculated using $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for all the homopolymers synthesized indicated that the tacticity remains the same as for other ATRP catalysts.

Chapter 4 contains the NMR studies of methyl methacrylate / n-butyl acrylate (M/B) copolymers synthesized by ATRP. Methyl 2-bromo propionate was used as the initiator with $\text{CuBr}/\text{Cu}(0)/N, N, N', N'', N'''$ -pentamethyldiethylenetriamine (PMDETA) as the catalyst at 60°C . Molecular weight distribution determined by GPC showed linear increase in M_n with conversion indicating towards a controlled polymerization and low Polydispersity Index (PDI) ($1.1 < M_w/M_n < 1.4$). Copolymer compositions (F_M) were calculated from ^1H NMR spectra. Reactivity ratios calculated using Mao-Huglin terminal model at high conversion were found to be $r_M = 2.17$ and $r_B = 0.47$.

Using two-dimensional HSQC and TOCSY experiments, compositional and configurational sequence assignments for M/B copolymers were done. Carbon resonances of α -methyl group were assigned upto triad level of compositional sensitivity. Methine carbon region of n-butyl acrylate was assigned upto triad level of compositional sensitivity based on the 2D HSQC spectral analysis. The methylene carbon and proton resonances were assigned up to tetrad level of compositional and configurational sensitivity. The assignments were further confirmed using 2D TOCSY experiments.

2D HMBC studies on these copolymer systems were helpful in the assignment of the carbonyl region. The completely assigned ^1H NMR spectra obtained using the 2D HSQC and 2D TOCSY NMR studies was utilized to make assignments in the 2D HMBC spectra.

The trend followed by F_M as the function of conversion indicated that there is a significant continuous change in the copolymer composition with conversion. i.e. synthesis of gradient copolymers. So, the variation in composition reflected in the concentrations of the dyad and triad fractions along with conversion were analyzed in methine, methylene and α -methyl carbon region.

Chapter 5 incorporates the synthesis of block copolymers of n-butyl acrylate and methyl methacrylate having targeted M_n ranging from 4000 to 60000 using ATRP. The aim was to compare the relaxation studies of block of lowest M_n (4300) with the higher block (30000) and to perform the structural investigations of the block copolymers using both 1D and 2D NMR spectroscopy.

P_m calculated for both the homopolymers and for block copolymer was found to be comparable indicating that the tacticity of block copolymer and that of statistical copolymer remains the same.

The structural investigations were also carried out on the same block copolymers to observe the BBM or BMM triads. The block having $M_n = 4300$ showed the presence of BBM triad in the carbonyl region in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The presence of this triad was confirmed by HMBC spectrum which showed the three bond order coupling between the carbonyl carbon of B unit with the backbone methylene of M unit.

T1 relaxation studies were performed at three different temperatures to observe the change in the internal motion with temperature. As expected, for all the side groups as well as for the main chain methylene, methine, carbonyl, quaternary and α -methyl carbon of homopolymers and the blocks, T1 increased with temperature. When comparison of the T1 relaxation values of the blocks with the corresponding homopolymers was made, it was found that although the backbone methylene (of M unit in the blocks) values were greater than PMMA, backbone methylene of B unit in the blocks showed values smaller than that of PBA. Similarly, the methine carbon of B unit of the blocks showed the decrease in value.

Chapter 6 contains the optimization of reaction conditions for the ATRP of N-vinyl carbazole. For synthesizing poly(N-vinyl carbazole) (PVK) under ATRP conditions, the choice of initiator was based on the fact that the structure of initiator should be similar with that of monomer so as to have efficient initiation. Hence we, proposed to use N-2-bromoethyl carbazole (NBC) as initiator. A series of test reactions were performed to optimize and standardize the reaction conditions using various combinations of copper halide and suitable ligands.

It was found that with the molar ratio $[\text{VCz}] : [\text{Cu(I)}] : [\text{Cu(II)}] : [\text{NBC}] : [\text{bpy}] = 100 : 1 : 0.3 : 1 : 3$ and ethylene carbonate as the solvent, 76 % monomer conversion was observed in 20 h. The trend of M_n and polydispersity (M_w/M_n) with percentage conversion for various $[\text{Cu(I)}]_0/[\text{Cu(II)}]_0$ showed that the polymerization proceeded in controlled manner. The effect of the addition of various initial concentration of deactivating species $[\text{Cu(II)}]_0$ on the kinetics,

semi-logarithmic plots $\ln[M]_0/[M]$ vs. reaction time i.e. both t and $t^{2/3}$ were plotted.

At 90°C, concentration of catalyst was reduced to 50% relative to initiator. As expected, the polymerization was slow but it was really very slow when compared to catalyst concentration of 1 equivalent relative to initiator

To demonstrate the presence of Br at the chain end of the homopolymer, PVK was used a macroinitiator i.e. methyl methacrylate monomer was added along with CuBr/bpy to a solution of PVK in ethylene carbonate at 70°C. The resulting copolymer was block PVK-b-PMMA giving a monomodal curve in the GPC. ^1H NMR of the polymer also confirmed the block structure.

Table of Contents

	Page No.
<i>Certificate</i>	i
<i>Acknowledgements</i>	ii
<i>Abstract</i>	v
<u>CHAPTER 1</u>	<u>INTRODUCTION</u>
1.1.	Introduction 1
1.2.	Polymerization Techniques 2
1.3.	Atom Transfer Radical Polymerization 3
1.3.1.	Mechanism and Kinetics 4
1.3.2.	Features of Atom Transfer Radical Polymerization 8
1.3.3.	ATRP Components 9
1.3.4.	Synthesis of new materials using ATRP 15
1.4.	Role of NMR in ATRP 16
	<i>References</i> 18
<u>CHAPTER 2</u>	<u>EXPERIMENTAL</u>
2.1.	Synthesis of Tetramethylguanidino-tris(2- aminoethyl)amine (TMG₃-TREN) 39
2.1.1.	Purification of reagents 39
2.1.2.	Procedure for synthesis 39
2.2.	Synthesis of tris(2- (dimethylamino)ethyl)amine (Me₆-TREN) 41

2.2.1.	Purification of reagents	41
2.2.2.	Procedure for synthesis	41
2.3.	Synthesis of N-2-bromoethylcarbazole	42
2.3.1.	Purification of reagents	42
2.3.2.	Procedure for synthesis	42
2.4.	Atom Transfer Radical Polymerization	43
2.4.1	Purification of reagents	43
2.4.2.	Synthesis of gradient copolymers of methyl methacrylate and n-butyl acrylate	44
2.4.3.	Synthesis of block copolymers of n-butyl acrylate and methyl methacrylate	45
2.4.4.	Homopolymerizations of methyl methacrylate, n-butyl acrylate, styrene and acrylonitrile using CuBr/ TMG ₃ -TREN as the catalyst.	46
2.4.5.	Homopolymerization of N-vinylcarbazole	46
2.5.	Characterization	47
2.6.	Reactivity Ratios determination and Simulations	48
2.7.	NMR Studies	50
2.7.1.	1D NMR measurements	50
2.7.2.	2D NMR measurements	50
2.7.3.	T ₁ Relaxation Studies	51
	<i>References</i>	<i>51</i>
<u>CHAPTER 3</u>	<u>ATRP USING CuBr/TMG₃-TREN AS CATALYSTS</u>	
3.1.	Introduction	53

3.2.	Polymerization of MMA with CuBr/TMG₃-TREN	55
3.3.	Polymerization of BA using CuBr/TMG₃-TREN	60
3.4.	Polymerization of styrene with CuBr/TMG₃-TREN	64
3.5.	Polymerization of acrylonitrile with CuBr/TMG₃-TREN	68
3.6.	Polymerization mechanism and Tacticity	72
3.7.	Conclusions	74
	<i>References</i>	<i>74</i>
<u>CHAPTER 4</u>	<u>GRADIENT COPOLYMERS</u>	
4.1.	Introduction	77
4.2.	Copolymerization of methyl methacrylate and n-butyl acrylate by ATRP	80
4.3.	Copolymer composition and Reactivity ratio determination	82
4.4.	Tacticity involved in ATRP	84
4.5.	¹³C{¹H} NMR studies	84
4.6.	Analysis of α-methyl region	86
4.7.	Analysis of methine region	90
4.8.	Analysis of backbone methylene region	94
4.9.	Analysis of carbonyl region	100
4.10.	Compositional drift analysis	106
4.11.	Conclusions	116
	<i>References</i>	<i>116</i>

CHAPTER 5 BLOCK COPOLYMERS

5.1.	Introduction	119
5.2.	Preparation and characterization of macroinitiator PBA-Br	121
5.3.	Preparation and characterization of PBA-b-PMMA block copolymers	125
5.4.	Analysis of tacticity	129
5.5.	2D NMR Analysis	130
5.6.	T ₁ Relaxation studies	134
5.7.	Conclusions	136
	<i>References</i>	136

CHAPTER 6 ATRP OF N-VINYLCARBAZOLE

6.1.	Introduction	139
6.2.	Choice of initiator	141
6.3.	Choice of catalyst system	141
6.4.	Optimization of [Cu(I)] ₀ /[Cu(II)] ₀ ratio	143
6.5.	Effect of [CuBr ₂] ₀ on the polymerization kinetics	145
6.6.	Effect of [NBC] ₀ on the polymerization kinetics	147
6.7.	Effect of minimum concentration of catalyst on the polymerization kinetics	150
6.8.	Effect of CuX (X = Br, Cl) on the polymerization kinetics	151
6.9.	Effect of Cu(0)/CuBr ₂ as catalyst on polymerization	153

6.10.	Analysis of the end group	155
6.11.	Polymerization mechanism by tacticity	158
6.12.	Conclusions	160
	<i>References</i>	<i>160</i>
	<i>Curriculum Vitae</i>	163