PREDICTION OF CARBON-13 CHEMICAL SHIFT VALUES AND 2D NMR STUDIES OF ACRYLONITRILE COPOLYMERS

by

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submitted
in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the

Indian Institute of Technology, Delhi

May, 2007

Dedicated to my parents

Certificate

This is to certify that the thesis entitled "**Prediction of carbon-13 chemical shift values and 2D NMR studies of acrylonitrile copolymers**" being submitted by **Jaspreet Kaur** to the Indian Institute of Technology, Delhi for the award of **Doctor of Philosophy** is a record of bonafide research work carried out by her. Jaspreet Kaur has worked under my guidance and supervision and has fulfilled the requirements for the submission of thesis which to my knowledge has reached the requisite standards.

The results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree / diploma.

14/5/07

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Acknowledgements

This work has been a journey of growth and development bundled with many challenges, failures and few rewarding experiences. During this, I have learned numerous new indispensable pieces of knowledge of contemporary science. All this has been a memorable experience for which I am grateful.

I would like to convey my supreme gratitude to my supervisor, Prof. A.S. Brar for presenting me the opportunity to work under his guidance. This thesis grew out of a series of dialogues with my supervisor Professor. His comments on papers and chapter drafts are in themselves a course in critical thought upon which I will always draw.

I am obliged to present and ex- Head of Department, Prof. B. Jayaram, Prof. U. K. Nadir for extending the funds and facilities essential for carrying out this research work.

I desire to take this opportunity to thank esteemed teachers, Dr. N. D. Kurur for teaching me NMR and Dr. Jayadeva of electrical engineering department for teaching and clearing my doubts related to neural networks.

Support of technicians especially Mr. Munnalal and non-teaching staff is really appreciated.

I can not articulate my feelings for my husband, Dr. Mukesh who with all the patience, understanding and love stayed with me in all the weathers. I want to thank him for making my life simple, easy and enjoyable; for making me more confident and for helping me in adjusting with his loving family.

I am forever grateful to my parents, whose foresight and values paved the way for the privileged education and for gently offering counsel and unconditional support at each turn of the road. I heartfully thank my sis Sandy for supporting me when ever I feel low and my bro Guki for his funny ways of making my life cool.

I wish to appreciate all of my batch mates and friends. I relished the company of all my labmates and juniors particularly of Gurmeet, Sukhi, Meghna, Tripta, Sonia, Pravin, Puneeta and Ashok. I wish to thank Sonia for all the support, company and entertainment she has provided during the last stages of my thesis.

In the last but not the least I want to thank almighty for showing me the right path.

Jaspreet Kaur

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Abstract

Copolymerization is the most eminent and powerful method for effecting systematic changes in polymer properties. It generally incorporates two or more different monomer bearing diverse physical and/or chemical properties and lead to the formation of new materials with immense scientific and commercial importance. It modulates both intra- and intermolecular forces exercised between like and unlike segments and hence the properties such as glass transition temperature, solubility, dyeability, adhesion, elasticity, crystallinity and chemical reactivity which may be varied within wide limits.

One of the simplest procedures for accomplishing copolymerization is free radical polymerization and it has two significant advantages first, it doesn't require rigorous experimental conditions and second it can be implemented to large variety of monomers.

Elucidation of copolymer structure (copolymer composition, monomer sequence distribution) is of foremost concern for the prediction of copolymer properties in addition to correlation between structure and properties. One of the main established functions of NMR in polymer science is the structural characterization of the copolymers, which provides the link between structure–property relationships. One dimensional NMR techniques (^{1}H, $^{13}C\{^{1}H\}$, DEPT etc.) in conjugation with two-dimensional techniques such as HSQC, TOCSY and HMBC provides a competent means for the stereochemical investigation of polymers. HSQC and HMBC techniques provide correlations between the resonances of ^{1}H and ^{13}C nuclei having one-(HSQC), two- or three-(HMBC) bond couplings. TOCSY in conjugation with HSQC provides one to one correlation between protons giving information about various vicinal and geminal couplings.

Chapter 1

This chapter submits the literature survey about the role of modern NMR spectroscopic techniques hitherto in the solution of complex structural elucidation problems of the contemporary polymer research. Here, we also presents the brief overview of the theoretical approaches utilized in prediction of carbon-13 NMR chemical shifts and hence the microstructure of copolymers.

Chapter 2

This chapter describes various computational (Back propagation algorithm used to predict the carbon-13 chemical shift values) and experimental protocols along with details of the conditions followed in homo and copolymerization of acrylonitrile monomer with methyl acrylate, ethyl acrylate, butyl methacrylate, 2-hydroxy ethyl methacrylate and 2-vinyl pyridine besides giving a brief account of various experimental techniques utilized throughout the current research work

The experimental details for recording of 1D (^{1}H, $^{13}C\{^{1}H\}$, DEPT-135, 90, quantitative carbon-13) NMR and 2D (heteronuclear single quantum correlation (HSQC), total correlation spectroscopy (TOCSY) and heteronuclear multiple bond correlation (HMBC)) NMR experiments are also incorporated. Furthermore, the details of the calculation of outfeed compositions and reactivity ratios are added.

Chapter 3

^{13}C NMR spectral simulation techniques can provide assistance in the solution of complex structural elucidation problems. These are based on the existence of direct yet complex relationship between the observed chemical shifts of carbon atom and its environment.

Herein, we have utilized artificial neural network (three layered neural network) for the to simulate the $^{13}C\{^{1}H\}$ NMR chemical shifts for the hydrogen terminated fragments of acrylonitrile copolymers and comparison was done with carbon-13 chemical shift values predicted by partial least square regression analysis (PLSR).

Here, to link molecular structure with the chemical shift values, an indirect approach was applied. This approach was realized in two steps:

(a) Representing each copolymer's molecular structure with numerical descriptors, which adequately describes the chemical environment.

(b) Choosing only those subsets of the descriptors which are information rich and building good models that can predict chemical shift value.

The generated models were cross-validated using leave-n-out method (n=1) of cross-validation. Each model was validated 50 times in order to obtain reliable statistics and establish the true generalization capabilities of resulting model. Neural Network gave mean absolute error (mae) =1.4 ppm (partial least square regression gave mae = 5.0 ppm) indicating that neural network can be used to predict carbon-13 NMR chemical shift information and hence microstructure of the copolymers.

Subsequently, the ^{13}C chemical shift values of methine and methylene carbon atoms of acrylonitrile/butyl methacrylate and acrylonitrile/ethyl acrylate copolymers were predicted with the average mean absolute error of various carbons varies between 0.4 to

1.3 ppm. The calculated chemical shift values have good correlation with the experimental values. The results were compared with partial least square regression method, which gave the error between 2.0-5.5 ppm.

Chapter 4

The copolymers of alkyl acrylate find their uses as binders, coating and paints etc. The incorporation of methyl acrylate to a suitable level in the copolymers of acrylonitrile reduces its melting temperature thus improving its processability. This chapter offers the studies carried out regarding the microstructure elucidation of Acrylonitrile/Methyl acrylate (A/M) and Acrylonitrile/Ethyl acrylate (A/E) copolymers. The A/M and A/E copolymers having different monomer compositions were synthesized using solution polymerization and the composition of resultant A/M copolymers was determined using quantitative $^{13}C\{^{1}H\}$ NMR. The values of reactivity ratios in case of A/M copolymer indicate that there is random placement of two monomers along the copolymer chain. The methine and methylene regions in $^{13}C\{^{1}H\}$ NMR spectrum of acrylonitrile–methyl acrylate copolymer were distinguished with the help of DEPT-135. Correlations between carbon and proton signals were obtained from the ^{1}H–^{13}C heteronuclear single quantum correlation (HSQC) of A/M copolymer. Methine carbons of A and M unit shows compositional as well as configurational sensitivity upto triad level. In order to establish various connectivities in the copolymer chain, the TOCSY spectra were recorded. Two and three bond coupling between protons of different groups that are directly coupled in A/M copolymer was seen in TOCSY experiment. Heteronuclear multiple-bond correlation spectroscopy has been used to study carbon (carbonyl/nitrile)–proton coupling. The carbonyl and nitrile carbons showed compositional sensitivity upto the triad level.

Acrylonitrile/Ethyl acrylate copolymers revealed similar trend in 1D and 2D NMR as exhibited by acrylonitrile and methyl acrylate copolymers.

Chapter 5

Synthetic polymers derived from functional methacrylates have been widely used in industry, agriculture and medicine owing to their remarkable properties such as potential biocompatibility. This chapter provides the detail description of the microstructure elucidation through sequentially assigned 1D and 2D NMR spectra of various acrylonitrile-(butyl and 2-hydroxy ethyl) methacrylate copolymers along with their composition and the reactivity ratios of monomers in these copolymers.

The copolymer compositions of acrylonitrile/butyl methacrylate (A/B) and acrylonitrile/2-hydroxy ethyl methacrylate (A/H) copolymers were ascertained from quantitative $^{13}C\{^{1}H\}$ NMR spectra by quantifying carbonyl and nitrile carbons. The values of reactivity ratio affirm that methacrylate monomers are more reactive than acrylonitirile monomer towards propagating chain.

The quaternary and methylene carbon-13 signals were found to be broad and overlapped. Hence, differentiated and recognized with the help of DEPT-135. Especial emphasis was given to the resonances of methine, α-methyl and methylene carbon which were rich in information about microstructure of copolymer. In HSQC studies, it was seen that the methine carbon/proton resonances showed both stereochemical and compositional sensitivity. By comparing the HSQC spectrum of polyacrylonirile with those of copolymers (A/B) of various compositions, it was noticed that the methine region was further splitted and A centered unit was assigned to AAA, AAB and BAB triads respectively. The spectral region attributed to AAA triad decreased in intensity as acrylonitrile content in the copolymer reduced. This triad region also exhibited configurational sensitivity and were assigned to ArArA, ArAmA and AmAmA triads respectively. The AAB triad showed further compositional sensitivity and was assigned to AAABA, AAABB and BAABB pentads. Out of which AAABA and AAABB were observed to be configurationally sensitive. These assignments were verified with the help of TOCSY. Similarly, by comparing the HSQC spectra of A/B copolymer of different compositions, BAB triad was assigned up to pentad level (ABABA, ABABB and BBABB). ABABA and ABABB pentad showed configurational sensitivity. The configurations in various pentads were affirmed via TOCSY. Methylene and α-methyl regions were similarly assigned with the help of HSQC upto triad, tetrad and pentad levels. In order to comprehend the connectivity and to ascertain various couplings in the copolymer chain, TOCSY spectra were recorded and assignments were done. Two and three bond coupling between protons of different groups that are directly coupled in A/B copolymer can be seen in TOCSY experiment at low mixing time. The methine protons in various triads and pentads exhibited three-bond coupling with the methylene protons of various dyads and tetrads.

Heteronuclear multiple-bond correlation (HMBC) has been employed to study carbon (carbonyl/nitrile)-proton coupling. The carbonyl and nitrile carbons expressed compositional sensitivity up to the triad level. HMBC reasserted the assignments done with 2D-HSQC and TOCSY experiments

Acrylonitrile/2-Hydroxy ethyl methacrylate: These acrylonitrile-methacrylate copolymers showed compositional sensitivity up to triad and tetrad level with meso and racemic configurations for methine, methylene and α-methyl resonances. Various 2D (HSQC, TOCSY, and HMBC) NMR techniques in conjugation with 1D (^{1}H, $^{13}C\{^{1}H\}$, and DEPT) NMR experiments have been exploited as an efficacious method for analysis of the microstructure of acrylonitrile-2-hydroxy ethyl methacrylate copolymers.

Chapter 6

Homo- and copolymers of 2-vinylpyridine has numerous remarkable applications such as stabilizers, catalysts, extractants, conductors etc. This chapter is based on the copolymers of 2-vinyl pyridine with acrylonitrile. The Acrylonitrile/2-vinylpyridine (A/V) copolymers were synthesized using bulk polymerization route. The values of reactivity ratio were obtained again using copolymer composition data by Kelen-Tudos and non linear error in variable methods. The assignments of carbon resonances were done with the help of $^{13}C\{^{1}H\}$ NMR and DEPT-135 spectra of A/V copolymer. Particular interest was given to the resonance of methine and methylene carbon signals which were rich in information about monomer unit sequence. Explicit information about compositional and configurational sequences was afforded by 2D HSQC in conjugation with TOCSY. Methine and methylene region depicted sensitivity towards both composition and configuration. HSQC showed compositional and configurational sensitivity of A, P centered unit of methine region up to the triad level while methylene region showed sensitivity to the dyad level.

TOCSY demonstrated two and three bond couplings between the protons of different directly coupled groups. HMBC experiment exhibited nitrile carbon couplings with the methine and methylene protons, HMBC in conjugation with HSQC and TOCSY strongly reaffirmed the assignments. Thus, methine and methylene regions were comprehensively analyzed by 2D-NMR (HSQC, TOCSY and HMBC) spectroscopy which appropriated ^{n}J (n = 1(HSQC), 2 and 3 (TOCSY and HMBC)) bond couplings detection.

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