ANALYSIS OF THE CARBON-13 NMR CHEMICAL SHIFTS AND 2D NMR STUDIES OF VINYL COPOLYMERS

by

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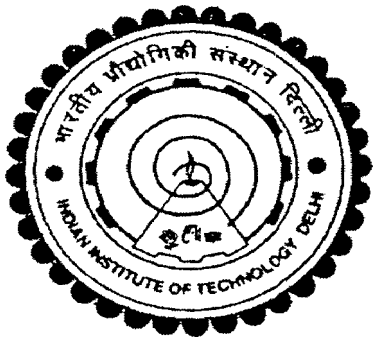

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To

His Holiness
Shri Satguru Jagjit Singh Ji

Certificate

This is to certify that the thesis entitled, "ANALYSIS OF THE CARBON-13 NMR CHEMICAL SHIFTS AND 2D NMR STUDIES OF VINYL COPOLYMERS", being submitted by Mr. Gurmeet Singh to the 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 him. Mr. Gurmeet Singh 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 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.

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Abstract

NMR spectroscopy with newer experiments and advancement of the instrumentation has become all the more an indispensable tool for a polymer chemist. NMR is the most widely used technique for qualitative and quantitative analysis of chain microstructure and polymer composition determination. It contributes valuable structural information, helping in deeper understanding of the polymer properties and thus permitting synthesis of polymers with required properties. Chemical shift is one of the spectral parameter characterizing the chemical environment of a carbon nucleus. Being a sensitive probe for environment of carbon atoms, ^{13}C NMR chemical shift plays a central role in NMR spectroscopy for solving structural problems. 2D NMR has emerged as the most effective technique for the study of the polymer structure.

A detailed analysis of the copolymer spectra enables the determination of comonomer sequence distribution and reactivity ratios. Owing to the complexity of copolymer spectra, complete assignments are a difficult task. Nevertheless, because of the high information content of fully interpreted spectra, it remains an important area to investigate. In the research work incorporated in the thesis, a sequential approach based on the reactivity ratios determination, chemical shift modeling, spectral simulation and 2D NMR spectral analysis has been applied for the microstructure analysis of polymers. Genetic Algorithm has been applied for the optimization of the reactivity ratios and chemical shift additive parameters.

The thesis consists of five chapters. The work done in the field "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 the polymer microstructure, with special emphasis on the sequence distribution is included. The theoretical basis of the, reactivity ratios optimization, the models used for the chemical shift modeling and Real Coded Genetic Algorithm has been explained.

The ***Chapter 2*** contains the synthetic details of the free radical and photo polymerization of the homopolymers and copolymers. The experimental details for the 1D ^{1}H, $^{13}C\{^{1}H\}$, 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 working of the real coded genetic algorithm, details of the selection, crossover and mutation operators and coding are specified. The theoretical basis and the experimental details about the optimization of the reactivity ratios from the infeed/outfeed fractions, dyad and triad fractions using the least square methodology are given. The details of the calculations of resonance signals' intensities, chemical shift modeling and simulation of NMR spectra are specified.

Chapter 3 contains the structural investigations of PMMA (poly(methyl methacrylate)) by NMR spectroscopy. Previous assignments made by some of the authors for methylene carbon resonances differed and a need was felt for critical analysis of the long range carbon/proton couplings by 2D HMBC spectrum in tandem with HSQC and TOCSY spectral analysis. For the free radically synthesized PMMA, pentads sequences mmrr and rmrm (where m and r represent the meso and racemic placement of the monomer units, respectively) of the carbonyl carbon resonances, having equal intensities were difficult to be

distinguished. To resolve these resonances, empirical chemical shift modeling was done. The chemical shift additive parameters obtained from the empirical chemical shift modeling of carbonyl carbon resonances were optimized by Genetic Algorithm which enabled unequivocal assignments of the resonances.

Rigorous assignments of the methylene carbon and proton resonance signals were made by investigating the one bond couplings between $^{1}H/^{13}C$ nuclei by the 2D HSQC spectroscopy and two bond $^{1}H/^{1}H$ couplings by the 2D TOCSY experiments. Analysis of the two and three bond order $^{1}H/^{13}C$ couplings of methylene protons with α-methyl, carbonyl carbon, quaternary and methylene carbon resonances was carried out from 2D HMBC spectrum enabling to substantiate the assignments of the methylene carbon and proton resonances at tetrad level of configurational sensitivity. Investigations of the couplings between carbonyl carbon with methylene protons and α-methyl carbon resonances conform to the results obtained from the chemical shift modeling.

Chapter 4 contains NMR studies of the vinylidene chloride copolymers. Vinylidene chloride copolymers because of the gas and vapor impermeability find applications as membranes in molding resins, rigid barrier containers, and etc. Microporous and mesoporous activated carbons obtained from vinylidene chloride copolymers act as effective adsorbent for water purification, gas separation and as support materials in catalysis systems. Microstructure analysis of the vinylidene copolymers can thus give a better insight to their physical properties.

Analysis of the quaternary carbon resonance signals of vinylidene chloride in vinylidene chloride (V) / methyl acrylate (M) copolymers at pentad level of compositional sensitivity is presented in this chapter. An approach based on

calculation of intensities of resonances, chemical shift modeling and spectral simulation has been used for the analysis of overlapped resonances. The reactivity ratios were optimized from the triad and diad fractions. The assigned resonances were modeled into empirically additive chemical shift parameters and the optimized additivity parameters were used to predict the chemical shifts of the overlapping resonances. Comparison of the intensities of pentad resonances assigned by chemical shift modeling and experimental intensities of resonances was done to ascertain the assignments made.

The microstructure analysis of vinylidene chloride (V) / vinyl acetate (A) copolymer system was done by chemical shift modeling, spectral simulation and 2D NMR spectroscopy. Chemical shift modeling was applied to analyze the compositionally sensitive resonances of quaternary carbon of vinylidene chloride unit. Reactivity ratios were optimized from the diad and triad fractions. The chemical shift modeling of the assigned quaternary resonances enabled prediction of the chemical shifts of the unassigned overlapping resonances at the pentad level. To resolve the complex ^{1}H and $^{13}C\{^{1}H\}$ spectra of copolymers, 2D $^{1}H/^{1}H$ TOCSY, $^{1}H/^{13}C$ HSQC and HMBC experiments were conducted. Methine proton resonances were assigned at the pentad level of compositional sensitivity. Methylene proton resonances were assigned up to the hexad level of compositional sensitivity. The combination of 2D NMR experiments supported by chemical shift modeling enabled us to assign the complex and overlapping proton and carbon-13 resonances unambiguously.

Analysis of the carbon-13 NMR chemical shifts of β-methylene of copolymers of vinylidene chloride with methyl acrylate, methyl methacrylate,

vinyl acetate, acrylonitrile, methacrylonitrile, acrylamide, styrene and methacrylic acid has been done. The analysis, based on the empirical additivity rules, propose chemical shift additive parameters for the monomer units in vinylidene chloride copolymers. Genetic algorithm has been applied for the optimization of additive parameters. Generalization of the analysis was done by optimizing the additive effects of the common functional groups (Cl, $COOCH_3$, CH_3, $OCOCH_3$, CN, $CONH_2$, C_6H_5 and COOH) present in the pendant groups, on the β-methylene carbon. The additive parameters successfully predicted the carbon-13 NMR chemical shifts of β-methylene of homopolymers and copolymers at tetrad level of compositional sensitivity. Vinylidene chloride copolymer systems having a large spread of β-methylene carbon chemical shift values proved to be good test subject for the chemical shift modeling of copolymers.

Chapter 5 incorporates the comprehensive microstructure analysis of methyl acrylate / methyl methacrylate copolymers by two-dimensional NMR spectroscopy. Methyl acrylate (A) / methyl methacrylate (B) copolymers of different compositions were synthesized and their compositions were determined from the ^1H NMR spectra. The reactivity ratios calculated using the least square methodology were $r_A = 0.32$ and $r_B = 2.63$ and calculated using non linear error-in-variables method with the RREVM computer program were $r_A = 0.32$ and $r_B = 2.61$. The reactivity ratios calculated from both the methods were in good agreement. Compositional and configurational assignments were done using 2D HSQC and TOCSY experiments. The methylene carbon and proton resonances were assigned up to the tetrad level of compositional and configurational sensitivity. The methine group of methyl acrylate was assigned up to the triad

level of compositional sensitivity for carbon resonances based on the 2D HSQC spectral analysis. The assignments were further confirmed using 2D TOCSY experiments. Carbon resonances of the α-methyl group were assigned up to triad level of compositional sensitivity from 2D HSQC spectra. The complexity in 1D NMR spectra precludes the assignments made evidently from the analysis of 2D HSQC and 2D TOCSY spectra. One to one correlation between carbon and proton resonances in the 2D HSQC spectra and cross-correlation peaks between nonequivalent protons in the 2D TOCSY experiments enabled us to assign the methylene, methine and α-methyl proton resonance signals in the overlapping ^{1}H NMR spectra unequivocally.

The methylene carbon and methine carbon resonances assigned from the 2D HSQC spectroscopy were established by analyzing the two and three bond couplings with α-methyl protons, methylene protons and methine protons from the 2D HMBC spectral analysis. Quaternary carbon resonances of the B unit were assigned by investigating the two bond couplings with α-methyl protons and methylene protons. Different assignments of carbonyl carbon resonances are available in the literature, prompting the experimental analysis of couplings of the carbonyl carbons with methylene protons and α-methyl protons from 2D HMBC spectral analysis to overcome any speculation of the assignments. Carbonyl carbon resonances were rigorously assigned by analyzing their couplings from the 2D HMBC spectra.

The 2D HSQC and TOCSY experiments in conjugation with the 2D HMBC experiments proved to be highly informative and irrefutable methodology for the microstructure analysis of polymers.

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