MICROSTRUCTURE DETERMINATION OF VINYLIDENE CHLORIDE COPOLYMERS BY ONE AND TWO DIMENSIONAL NMR SPECTROSCOPY

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Dedicated to....

My Husband

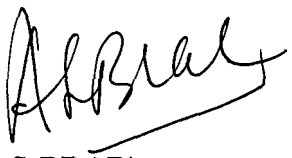
&

My Son

CERTIFICATE

This is to certify that the thesis entitled "**MICROSTRUCTURE DETERMINATION OF VINYLIDENE CHLORIDE COPOLYMERS BY ONE AND TWO DIMENSIONAL NMR SPECTROSCOPY**", being submitted by **Mrs. Meenakshi Malhotra** 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 her. Mrs. Meenakshi has worked under my supervision and guidance and has fulfilled all the requirements for the submission of this thesis which to our 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.



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ABSTRACT

Two important characteristics of polymers of vinylidene chloride are thermal instability and impermeability to wide range of gases and vapors. The present commercial success of these materials is due to the fact that the instability problem was overcome and barrier properties could be exploited by techniques such as copolymerization and plasticization developed by Ralph Wiley and co-workers. The commercialization of vinylidene chloride (VDC) polymers began in 1939 under the trademark saran. Of the many copolymers that have been prepared, only three types are commercially important. Vinylidene chloride-vinyl chloride copolymers, vinylidene chloride-alkyl acrylate and methacrylate coplymers and vinylidene chloride-acrylonitrile copolymers. The utility or the application of any polymer is dictated by its mechanical properties which in turn are under the control of composition, the molecular weight, morphology, defect structures, tacticity, branching and molecular motion of polymer, that is dependent on its microstructure. Thus there arises the need to characterize the polymers on a molecular level, which forms the major part of our study. The information obtained from microstructure can further be used to tailor the copolymer with desired physico chemical properties and also to give clues to the mechanism of polymerization.

For the microstructural investigation, the best technique available till date is Nuclear Magnetic Resonance (NMR) spectroscopy. Though 1D experiments can provide valuable information but most of the time it is difficult to make unequivocal signal assignments; to this end, the two dimensional NMR techniques especially homonuclear COSY and heteronuclear correlation spectroscopiés have been applied in determining the stereochemical and compostional sequences of number of polymer systems.

In this research work we have reported the compositional and configurational sequences of vinylidene chloride copolymers using ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, DEPT, HSQC and DQF-COSY experimental techniques. The molecular weights of these polymers were obtained from Gel Permeation Chromatography technique. The composition was determined from elemental analysis by Schoneger technique.

The thesis consists of five chapters. The first chapter gives the introduction to the microstructure, various models of polymerization, polymerization process and the copolymer equation. It gives the detailed survey of the literature on the vinylidene chloride copolymers. This also describes the use of NMR in establishing the microstructure of polymers.

The second chapter describes the experimental procedures for the preparation of homo- and co-polymers. Experimental detail of the molecular weight determined by GPC is given. It also describes the schoneger oxygen flask technique for quantitative estimation of chlorine contant in copolymers. Experimental conditions for recording of 1D and 2D NMR spectra are given in this chapter.

Third Chapter deals with sequence determination for copolymers of vinylidene chloride -alkyl acrylate (methyl, ethyl, butyl) copolymers (V/R) prepared by photopolymerization. The copolymer compositions were determined from chlorine content of the copolymers. The reactivity ratios were then determined by Kelen Tudos (KT) and non linear error in variables (EVM) method using the copolymer composition data. The reactivity ratios determined for vinylidene chloride- methyl acrylate copolymers are $r_V = 0.95 \pm 0.13$ and $r_M = 0.90 \pm 0.08$. The microstructure of these copolymers were determined from NMR spectroscopy using $^{13}C\{^{1}H\}$ NMR signals of quaternary carbon and methine carbon resonating signals for V- and M- monomeric units respectively. Monte carlo

simulations were also used to determine the triad fractions. These were then compared to the calculated triad fraction values and were found to be in good agreement with the values determined from NMR, which shows that it gives a better fit to the first order Markov model. A ^{13}C distortionless enhancement by polarization transfer spectrum (DEPT) was used to differentiate between the resonance signals methoxy and methylene units in the copolymer. 2D heteronuclear single quantum correlation (HSQC) was used to analyse the complex ^{1}H NMR spectrum and 2D DQF-COSY shows the various 1,3 and 1,2 bond interactions of the protons, thus giving a better insight for the copolymer microstructure. Similar studies were done for vinylidene chloride - ethyl acrylate and vinylidene chloride - butyl acrylate copolymers.

Fourth Chapter describes the microstructral studies for vinylidene chloride - alkyl methacrylates (methyl, ethyl, butyl) copolymers (V/R). For these copolymers the composition determined by schoneger oxygen flask method was used for determining its reactivity ratios by KT and EVM methods. The reactivity ratios found were $r_V = 0.26 \pm 0.04$ and $r_{M'} = 2.88 \pm 0.23$ for vinylidene chloride - methyl methacrylate copolymers. For this copolymer system, the $^{13}C\{^{1}H\}$ NMR signals were assigned based on the poly(methyl methacrylate) spectrum and it was observed that for α - methyl and carbonyl carbon resonance signal there is a compositional overlap of signals, hence these resonanting signals could not be used for making any quantitative estimation. The quaternary carbon resonating signals of methyl methacrylate unit were used for studying the copolymerization mechanism as the triad compositions were well separated. To determine the triad fractions of V-unit the quaternary carbon resonanting signal was used which was very well distinguished. The triad fractions thus obtained were compared with theoretically determined triad fractions. Monte carlo simulation were also used for determining the triad fractions and for studying the

variation of V- and M'- centred triads as a function of fractional conversion. 2D- HSQC and DQF-COSY experiments have been used for making various compostional and configurational assignments of these copolymers. The overlap of methoxy carbon with the methylene carbon was distinguished using DEPT carbon- 135 NMR spectrum. The methylene resonating signals are well separated and hence been assigned upto the tetrad level on the HSQC spectrum. The further splittings on ^1H NMR spectrum were assigned to different environment experienced by the two protons attached to the same carbon. This was confirmed by 2D DQF-COSY spectrum which showed the 1,2 bond geminal interactions in the methylene tetrads. Then for the α- methyl carbon region of M'- monomeric unit which was expected to have the compositional overlap is confirmed by the HSQC experiments. The HSQC was recorded for extreme compostions and it was observed from the variations in the intensity of the signals that triads of this region were overlapped on $^{13}C\{^1H\}$ NMR spectra whereas clearly separated on ^1H NMR.

Fifth Chapter is devoted to the copolymers of vinylidene chloride with vinyl acetate and vinyl propionate. The composition was obtained from the elemental analysis of chlorine, and from carbon-13 experiments. These data were then used for determining the reactivity ratios by KT and EVM methods. The reactivity ratios found were $r_V = 4.83 \pm 1.11$ and $r_A = 0.06 \pm 0.05$ for vinylidene chloride - vinyl acetate (V/A) copolymers. The copolymer mechanism was determined using the triad concentration calculated from the carbonyl and quaternary carbon resonating signals of A- and V- monomeric unit. V/A copolymer system gave a better fit to the First order Markov model. The various compositional sequences were assigned with the help of HSQC spectrum. The methine carbon resonance signal which was not clearly distinguished on $^{13}C\{^1H\}$ NMR was shown to be well separated on ^1H NMR by HSQC. All the cross peaks in the 2D- COSY have been assigned to the couplings between the methine and the methylene protons.

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