# SEQUENCE DETERMINATION OF ACRYLONITRILE COPOLYMERS BY ONE AND TWO DIMENSIONAL NMR SPECTROSCOPY

*By*

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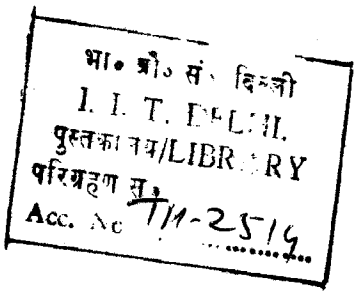


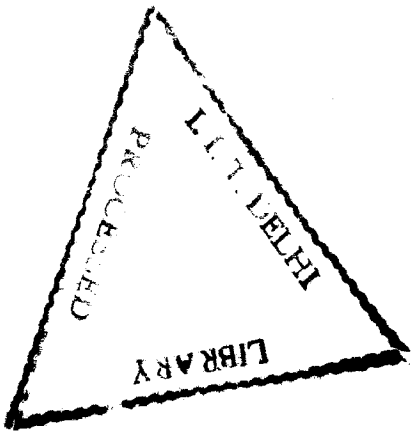

*With love,*

*to Sir, My Parents*

*&*

*all those who care for me . . .*

## CERTIFICATE

This is to certify that the thesis entitled,"**SEQUENCE DETERMINATION OF ACRYLONITRILE COPOLYMERS BY ONE AND TWO DIMENSIONAL NMR SPECTROSCOPY**", being submitted by **Mr. Kaushik Dutta** 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. Kaushik Dutta 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.

28/7/97

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**ABSTRACT :**

Homo- and copolymers of acrylonitrile are of great interest in many industrial applications e.g. as adhesive, binders, antioxidants, viscosity index improvers, dyes, emulsifying agents, insecticides, plasticizers, artificial organs, crosslinking agents, etc. Such a wide range of applications arises from the wide range of physical and chemical properties that can be covered by an appropriate choice of side groups and copolymer system. The physical and the chemical properties proved to be influenced fundamentally by the microstructure of these polymers, which involves the character of monomer distribution in the polymer chain and the stereochemical and compositional arrangements of various monomer units. The information concerning the microstructure of a polymer is also essential for clarifying the polymerisation mechanism.

So far numerous studies on the stereoregularity of poly(acrylonitrile) have been carried out by various workers. Scheafer, Inoue and Kamide et al. have reported the microstructure of poly(acrylonitrile) using $^{13}C$ NMR spectroscopy. Various worker have reported the microstructure and sequence distribution of acrylonitrile copolymers. Acrylonitrile - alkyl acrylates and methacrylates have been widely studied. Ritchey et al. assigned the acrylonitrile -alkyl methacrylate copolymer by $^{13}C\{^{1}H\}$ NMR spectroscopy. O'Donnell[6] et al. have analyzed the acrylonitrile - styrene copolymers for sequence distribution using the 13C NMR spectroscopy.

Keeping in view the significance of the polymer microstructure, a work was undertaken with a purpose to develop the theoretical and experimental basis for characterizing the structure of acrylonitrile copolymer 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 assignment; to this end, the two dimensional NMR techniques especially homonuclear COSY and heteronuclear (inverse HETCOR) correlation spectroscopies 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 configuration sequences of Acrylonitrile copolymers using one dimensional ($^1H$, $^{13}C\{^1H\}$ NMR and DEPT) and two dimensional (DQFCOSY, TOCSY, inverse-HETCOR, inverse-HETCOR-TOCSY and NOESY) experiments.

The thesis consists of six 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 monomers, homopolymers and copolymers. Experimental detail of the molecular weight determined by GPC is given. The copolymer composition of the acrylonitrile copolymers were determined from nitrogen analysis. This chapter also gives the detailed description of all the one and two dimensional NMR experiments carried out throughout this research work.

The third chapter deals with the sequence determination of the acrylonitrile / acrylic acid (A/B) and acrylonitrile / methacrylic acid (A/M) copolymers. The copolymers of acrylonitrile / acrylic and methacrylic acid were prepared by photo polymerization using uranyl ion as a photo sensitizer. The copolymer composition was determined from 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 of A/M copolymers are $r_A = 0.135 \pm 0.04$ and $r_M = 3.618 \pm 0.49$. The microstructure was obtained in terms of the distribution of A- and M- centered triad sequences from $^{13}C\{^1H\}$-NMR spectra of the copolymers. Homonuclear 2D TOCSY NMR was used to simplify the complex $^1H$ NMR spectra of A/M copolymer in terms of configurational / conformational sequences. The TOCSY experiments was used to make unambiguous assignments at the tetrad level of the methine proton in the $^1H$ spectra NMR of A/M copolymers. The reactivity ratios evaluated from composition data provide more accurate values than those evaluated from triad fractions. There is good agreement between the experimentally obtained (NMR) triad fractions and those calculated from theoretical models and MC simulations. Similarly, the triad sequence distribution of A/B copolymers were determined, in terms of A and B centered triads from $^{13}C\{^1H\}$ NMR spectra of the copolymers. The reactivity ratios determined from the compositional data by the EVM method are $r_A = 0.98$ and $r_B = 3.79$. The copolymerization mechanism, using the carbonyl and nitrile carbon resonances, was found out to follow first order Markov model. The carbon 13 NMR spectrum was completely assigned using the DEPT spectrum. The complex proton NMR spectrum was assigned to compositional triad fractions with the help of inverse HETCOR and DQFCOSY spectra. There is good agreement between the theoretically calculated and experimentally determined (NMR) triad fractions. The Monte Carlo simulation (MC) was used to study the effect of degree of polymerization on the triad fractions.

The microstructure of the acrylonitrile / alkyl methacrylates are given in chapter 4. The chemical microstructure of acrylonitrile / alkyl methacrylate (alkyl = pentyl, hexyl and heptyl) copolymers prepared by photopolymerization using uranyl ion as photo sensitizer were analyzed by $^{13}C\{^1H\}$ NMR spectroscopy. The composition of the copolymers were

determined by elemental analysis and comonomer reactivity ratios were determined by the Kelen Tudos (KT) and Error in Variable (EVM) methods. The reactivity ratios of acrylonitrile / pentyl methacrylate are $r_A$ = 0.20 and $r_P$ = 2.62. The complete spectral assignment of the overlapping proton and carbon spectra of these copolymers were done with the help of Distortionless Enhancement by Polarization Transfer (DEPT) and two dimensional $^1H$-$^{13}C$ heteronuclear shift correlation (inverse HETCOR) and 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. Monte Carlo simulation was used to study the effect of the degree of polymerization on the triad fractions. The microstructure of the acrylonitrile - hexyl methacrylate copolymers was determined with the help of the $^{13}C\{^1H\}$ NMR spectroscopy. It was found that the acrylonitrile / hexyl methacrylate copolymer system gave a better fit to second order Markov model than to the first order Markov model.

The fifth chapter deals with the microstructure determination of the poly(pentyl acrylate) homopolymer and acrylonitrile / alkyl acrylate (alkyl = pentyl, hexyl and heptyl) copolymers. The stereochemical structures of poly(pentyl acrylate) (PPA) prepared by solution polymerization is studied by the combination of one and two dimensional NMR Spectroscopy. The $OCH_2$, methine, methylene and the carbonyl carbon resonances are assigned to triad, tetrad and pentad sequences respectively. The polymerization mechanism was studied using the carbonyl and $OCH_2$ resonances. It was found that homopolymerization followed Bernoullian statistics. The various configurational assignments in the aliphatic region were done with the help of inverse HETCOR, inverse HETCOR-TOCSY, homonuclear DQFCOSY and TOCSY experiments. The microstructure of the acrylonitrile

/ alkyl acrylates copolymers were determined using the nitrile and carbonyl carbon resonances. The various compositional sequences have been assigned with the help of the one and two dimensional NMR spectroscopy. The proton NMR spectra of these copolymers are assigned with the help of inverse HETCOR experiments. The reactivity ratios of these copolymers were determined from KT and EVM methods using the copolymer composition data, which were obtained from the nitrogen analysis of the copolymers.

Copolymers of glycidyl methacrylate are increasing in importance due to their application as speciality copolymers for binding enzymes and microelectronics etc. The sixth chapter is devoted to the determination of reactivity ratios and microstructure of acrylonitrile / glycidyl methacrylate copolymers. The copolymer composition was determined from the nitrogen analysis of the copolymers. The reactivity ratios of the A/G copolymers, calculated from the EVM method are $r_A = 0.22$ and $r_G = 1.44$. The copolymer mechanism was determined using the triad concentration calculated from the nitrile and carbonyl carbon resonances. It was found that the A/H copolymer system gave a better fit to first order Markov model. The various carbon resonance signals were assigned with the help of DEPT NMR experiments. The various compositional sequences were assigned with the help of inverse HETCOR. All the crosspeaks in the DQFCOSY and TOCSY spectrum have been assigned to the couplings between the methine and the methylene protons.

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