STRUCTURAL INVESTIGATION OF VINYL TERPOLYMERS BY NMR SPECTROSCOPY

by

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Terpolymers,
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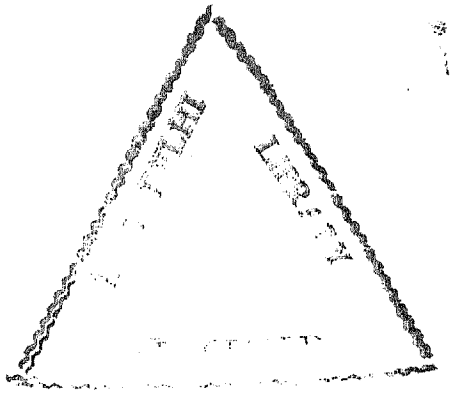

DEDICATED

TO

MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled, **"STRUCTURAL INVESTIGATION OF VINYL TERPOLYMERS BY NMR SPECTROSCOPY"**, being submitted by **Mr. Dev Ranjan Pradhan** 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. Dev Ranjan Pradhan 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 thesis has not been submitted, in part or full to any other University or Institute for the award of any degree or diploma.

12/5/03

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Dev ranjan Pradhan

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ABSTRACT

Vinyl homo- and copolymers are of great interest in many industrial applications e.g. as adhesive, binders, antioxidants, viscosity index improvers, emulsifying agents, crosslinking agents, etc.[1] There is growing interest in the enhancement of the properties e.g. mechanical, resistance to heat and radiation, optical activity, dyeability, vulnerability, flow behaviour etc. Therefore, it is worthy to synthesize a multicomponent system, wherein each monomer contributes some particular property.

A wide variety of chemical or physical strategies including copolymerization, polymer blends and crosslinking network have been explored to match the individual requirements.[2] Terpolymerization have continued to evoke interest not only in academics but also in industry[3], e.g. as macromolecular drugs, macromolecular catalysts, artificial organs 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 in terpolymers. The physical and the chemical properties proved to be influenced fundamentally by the microstructure of homo-, co-, and terpolymers, which involve the nature of monomer distribution, stereochemical and compositional arrangements of various monomer units in the polymer chains. Harwood et al.[4] have reported the sequence distribution in methyl methacrylate / methyl acrylate copolymers. Brar et al.[5-8] have determined the microstructure of methacrylonitrile / methyl methacrylate, methacrylonitrile / glycidyl methacrylate, acrylonitrile / styrene copolymers and acrylonitrile / styrene / methyl methacrylate terpolymer. The information obtained from the microstructure can further be used to synthesize the new terpolymers with the desired physicochemical properties.

Keeping in view the significance of the polymer microstructure, a work was undertaken with a purpose to develop the statistical and experimental basis for investigating the structure of vinyl terpolymer chains at molecular level. The stereochemical[9-11] and compositional[12, 13] structure of homopolymers and copolymers were investigated by one and two-dimensional NMR spectroscopy. One-dimensional experiments were not always suitable for unequivocal signal assignments. Therefore, the two-dimensional NMR techniques, especially, Heteronuclear Single Quantum Correlation (HSQC) and Total correlated Spectroscopy (TOCSY) have been applied in determining the stereochemical and compositional sequences. In this research work, the attempt has been made to determine the compositional and configuration sequences of vinyl terpolymers using one-dimensional (^{1}H, ^{13}C{^{1}H} NMR and DEPT) and two-dimensional (HSQC, TOCSY and NOESY) experiments.

The thesis consists of **six chapters.** The **first chapter** deals with the general introduction about the microstructure and the review of the literature. It describes the use of two-dimensional NMR spectroscopy for sequence determination.

The **second chapter** describes the experimental procedures for the preparation of homopolymers, copolymers and terpolymers. Experimental details of the molecular weight determined by GPC are given. The compositions of the copolymers and terpolymers were determined from quatitative ^{13}C{^{1}H} NMR spectroscopic technique. This chapter also includes the detailed description of the entire one and two-dimensional NMR experiments carried out throughout this research work.

The **third chapter** deals with the microstructure determination of the acrylonitrile / styrene / acrylic acid (N/S/A) terpolymers. These terpolymers were prepared by bulk

polymerization using benzoyl peroxide as initiator. The compositions of terpolymers were determined by quantitative $^{13}C\{^1H\}$ NMR spectra and compared with those calculated by Goldfinger's equation[14, 15] using comonomer reactivity ratios: $r_{NS} = 0.04$, $r_{SN} = 0.35$; $r_{NA} = 0.81$, $r_{AN} = 2.99$; $r_{SA} = 0.80$, $r_{AS} = 0.10$. All the assignments were done on the basis of the respective homopolymers and N/S, S/A, N/A coplymers and on the basis of change in variation of the intensity of signals with the copolymer compositions. The α-methine carbon resonances of S- and A- monomeric units are overlapping with the β-methylene carbon resonances of N-, S- and A- units. This overlapping carbon resonances were resolved with the help of DEPT-135 and DEPT-90 experiments. The Complete spectral assignments of $^{13}C\{^1H\}$ and ^1H NMR spectra were done with the help of two-dimensional ^{13}C-^1H Heteronuclear Single Quantum Coherence (HSQC). The assignments done for β-methylene group using HSQC technique are further confirmed by observing the crosspeaks due to vicinal coupling of methine proton with methylene protons in various dyads in TOCSY NMR spectra. 2D NOESY was used to ascertain the spatial proton- proton couplings.

The compositional assignments of the acrylonitrile / styrene / glycidyl methacrylate (N/S/G) terpolymers are given in **chapter four**. The terpolymers compositions were determined by quantitative $^{13}C\{^1H\}$ NMR spectra and compared with those calculated by Goldfinger's equation using comonomer reactivity ratios: $r_{NS} = 0.04$, $r_{SN} = 0.40$; $r_{NG} = 0.22$, $r_{GN} = 1.37$; $r_{SG} = 0.44$, $r_{GS} = 0.53$. The α-methine carbon resonances of N- monomeric unit are overlapping with the α-methyl carbon of G- unit. Further, the α-methine carbon of S- unit and epoxy methine carbon of G- unit are overlapping with the epoxy methylene carbon of G- unit and β-methylene carbon resonances of N-, S- and

G- units. The signal due to quaternary carbon of G- unit is also overlapping with the methylene carbon resonances of the terpolymer. These overlapping carbon resonances can be assigned without ambiguity with the help of DEPT-135 and DEPT-90 experiments. The carbonyl and quaternary carbon resonances are assigned to triad compositional sequences from the $^{13}C\{^1H\}$ NMR spectra. The methyl, methine and oxymethylene carbon resonances are assigned to triads, whereas the methylene carbon resonances are assigned to dyads compositional sequences with the help of 2D-HSQC spectra. The homonuclear 2D (^1H-^1H) TOCSY spectra suggested the various structural arrangements of the polymer chains. 2D NOESY spectrum is used to assign the spatial interaction between the aromatic protons and the methylene protons of respective triads and dyads.

The **fifth chapter** is devoted to the microstructure of the methacrylonitrile / methyl methacrylate (N/M) copolymer, methacrylonitrile / styrene (N/S) copolymer and methacrylonitrile / styrene / methyl methacrylate (N/S/M) terpolymer. The copolymer and terpolymer compositions were determined by quantitative $^{13}C\{^1H\}$ NMR spectra of individual copolymers and terpolymers. The terpolymer compositions were compared with those calculated by Goldfinger's equation using comonomer reactivity ratios: r_{NS} = 0.30, r_{SN} = 0.45; r_{NM} = 0.91, r_{MN} = 0.88; r_{SM} = 0.52, r_{MS} = 0.47. The comonomer reactivity ratios were determined by both Kelen Tudos (KT) [16] and non-linear error in variables (EVM) [17] methods using the copolymer composition data. The reactivity ratios of N/S copolymers are $r_N = 0.30 \pm 0.04$, $r_S = 0.45 \pm 0.05$ and $r_N = 0.29$, $r_s = 0.45$ respectively, whereas the reactivity ratios of N/M copolymers are $r_N = 0.91 \pm 0.09$, $r_S = 0.88 \pm 0.11$ and $r_N = 0.85$, $r_s = 0.83$ respectively. The nitrile, carbonyl and methyl carbon resonances of the

N/M copolymer are assigned to triad compositional and configurational sequences. In case of N/S/M terpolymer, the carbonyl and quaternary carbon resonance signals are complex and it was difficult to assign. The complex and overlapped ^{1}H and $^{13}C\{^{1}H\}$- NMR spectra of N/M and N/S copolymers and N/S/M terpolymers were resolved without ambiguity with the help of DEPT, 2D(HSQC, TOCSY) NMR techniques. The α-methyl, methine and methylene carbon resonances of the N/M and N/S copolymers were assigned upto triad and tetrad compositional and configurational sequences with the help of 2D-HSQC spectra. In the case of N/S/M terpolymers, the α-methyl, methine and methylene carbon resonances were assigned upto the compositional dyads and triads level. TOCSY spectra were used to assign the various vicinal and geminal couplings between the inequivalent methylene and methine protons of the copolymers and terpolymers.

The **chapter six** describes the sequence distribution of methacrylonitrile / butyl acrylate (M/B) copolymer, methacrylonitrile / vinylidene chloride (M/V) copolymer and methacrylonitrile / vinylidene chloride / butyl acrylate (M/V/B) terpolymers. The quantitative $^{13}C\{^{1}H\}$ NMR spectroscopic technique was used to determine the compositions of copolymers and terpolymers. The terpolymer compositions were compared with the theoretical values obtained from Alfrey-Goldfinger's equation using the comonomer reactivity ratios: $r_{MV} = 2.47$, $r_{VM} = 0.40$, $r_{MB} = 2.31$, $r_{BM} = 0.61$, $r_{VB} = 0.91$ and $r_{BV} = 0.89$. The reactivity ratios were determined by Kelen Tudos (KT) and non-linear error in variables (EVM) methods are $r_M = 2.31 \pm 0.08$, $r_B = 0.61 \pm 0.03$ and $r_M = 2.23$, $r_B = 0.58$ respectively for M/B copolymers and $r_M = 2.47 \pm 0.14$; $r_V = 0.40 \pm 0.02$ and $r_M = 2.43$; $r_V = 0.39$ respectively for the M/V copolymers. The nitrile, quaternary, methyl and methylene carbon resonances of the M/V copolymers were assigned to triad

and tetrad compositional sequences, while methine carbon resonances of M/B copolymers were assigned to triad compositional sequences. The overlapping methine and methylene carbon resonances of the M/B copolymer and M/V/B terpolymers were differentiated by DEPT experiments. The quaternary carbon resonances of the M/V/B terpolymers were assigned to triad compositional sequences. The complete ^{1}H and $^{13}C\{^{1}H\}$- NMR spectra of M/B, M/V copolymers and M/V/B terpolymers were assigned without any ambiguity with the help of 2D(HSQC, TOCSY) NMR spectroscopic techniques.

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