SEQUENCING OF N-VINYL-2-PYRROLIDONE COPOLYMERS BY NMR SPECTROSCOPY

by

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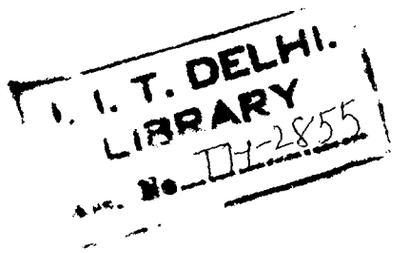

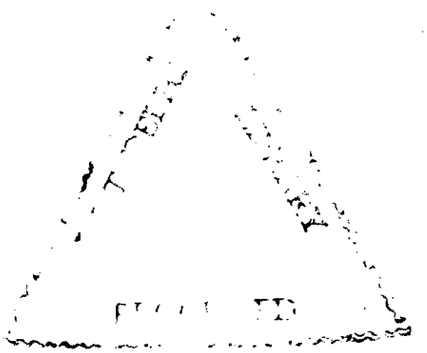

Dedicated

To

My Parents

CERTIFICATE

This is to certify that the thesis entitled, **"SEQUENCING OF N-VINYL-2-PYRROLIDONE COPOLYMERS BY NMR SPECTROSCOPY"**, being submitted by **Mr. Rajeev Kumar** 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. Rajeev Kumar 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.

4/3/2002

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(Rajeev Kumar)

ABSTRACT

N-vinyl-2-pyrrolidone polymer has biocompatiability as well as good film forming and adhesive characteristics. It is frequently used as a comonomer mainly because of its amphiphilic character. It contains a highly polar amide group, which is responsible for its hydrophilicity and polar group attracting properties while the methylene and the methine groups in the main and side chain is responsible for the hydrophobic properties. The homo and copolymers of N-vinyl-2-pyrrolidone are of great interest in many industrial applications e.g. as adhesive, binders, tablet coatings, in the membranes for ultrafiltration, emulsifying agents, soft contact lenses, light-sensitive coatings for lithographic printing plates etc. Such a large range of applications arises from the large range of physical and chemical properties. This can be covered by an appropriate choice of side groups and copolymer system. The properties of these polymers are fundamentally influenced by their microstructure, which involves the monomer sequence distribution in the polymer chain and the compositional and configurational arrangements of the monomer units. The information obtained from the microstructure can further be used to synthesize the copolymer with the desired physico-chemical properties and to give information about the mechanism of copolymerization. NMR spectroscopy has been found to be the most reliable technique for characterization of the configurational structures of the polymers, because the chemical shift is sensitive to configurational sequences.

The study of the stereoregularity of poly(N-vinyl-2-pyrrolidone) have been carried out by various workers. Brar et al. have reported the configurational assignments

of poly(N-vinyl-2-pyrrolidone) using one and two-dimensional NMR spectroscopy. The microstructure and sequence distribution of N-vinyl-2-pyrrolidone copolymers has been reported by many workers. Price et al. and Reddy et al. synthesized and characterized the N-vinyl-2-pyrrolidone / glycidyl methacrylate copolymers by $^{13}C\{^{1}H\}$ NMR spectroscopic techniques. Gatica et al. have reported the synthesis and reactivity ratios of N-vinyl-2-pyrrolidone with vinylpyridine by carbon NMR spectroscopy.

Due to the importance of the microstructure in the polymers, this research work was carried out to develop the theoretical and experimental basis for characterizing the structure of N-vinyl-2-pyrrolidone copolymer chains at molecular level. 2D NMR spectroscopy have been used as the most effective method for determining the compositional and conformational sequences of the copolymers. Traditional techniques (1D NMR spectroscopy) were not always suitable for unequivocal signal assignment. This necessitates the use of two-dimensional NMR techniques, especially Heteronuclear Single Quantum Correlation (HSQC) in determining the compositional and stereochemical sequences.

In our present research work the microstructure of N-vinyl-2-pyrrolidone with acrylonitrile, methacrylonitrile, glycidyl methacrylate, methyl methacrylate, methyl acrylate, butyl acrylate and vinyl acetate copolymers have been determined by one dimensional (^{1}H, $^{13}C\{^{1}H\}$ NMR and DEPT) and two dimensional (HSQC, TOCSY and NOESY) NMR experiments.

The thesis is divided into six chapters. The **first chapter** explains the general introduction about the microstructure of the polymers and the literature survey of the

copolymers especially N-vinyl-2-pyrrolidone copolymers. It also explains the use of one and two dimensional NMR spectroscopy for the determination of the microstructure.

The experimental procedures for the preparation of homopolymers and copolymers are described in the **second chapter**. The experimental details of the techniques used for the molecular and compositional characterization were also given in this chapter. Gel Permeation Chromatography (GPC) was used to determine the molecular weight of the copolymers. The copolymer composition for the N-vinyl-2-pyrrolidone copolymers was determined from ^{1}H-NMR, quantitative $^{13}C\{^{1}H\}$ NMR spectra and C, H, N elemental analysis. The comonomer reactivity ratios were determined by both Kelen-Tudos (KT) and non-linear least-square error-in-variables model (EVM) methods. This chapter also includes the description of all one and two-dimensional NMR experiments carried out throughout this research work.

The sequence determination of the N-vinyl-2-pyrrolidone / acrylonitrile (*V/A*) and N-vinyl-2-pyrrolidone / methacrylonitrile (*V/N*) copolymers is described in the **third chapter**. The copolymer composition was obtained using the quantitative $^{13}C\{^{1}H\}$ NMR spectra. The reactivity ratios of *V/A* copolymers was found to be $r_V = 0.06 \pm 0.01$ and $r_A = 0.46 \pm 0.02$. The *V*- and *A*- centered triad concentrations were calculated from $^{13}C\{^{1}H\}$ NMR spectra of the copolymers. There was a good agreement between the experimentally obtained (NMR) triad fractions and those calculated from the first order Markov terminal model, using Harwood's program. DEPT (Distortionless Enhancement by Polarization Transfer) NMR spectrum was used to differentiate the resonance signals for the methine and methylene carbons in the copolymer. The methine (-CH) carbon resonance of *A* unit was assigned to pentad compositional sequences whereas the methine

resonance signals of *V* unit were assigned upto triad compositional sequences. The β-CH_2 was assigned to dyad sequences only. These compositional sequences were confirmed by applying the 2D Heteronuclear Single Quantum Correlation (HSQC) spectroscopy. 2D TOCSY NMR spectroscopy was used to simplify the complex ^{1}H NMR spectra. The TOCSY spectrum also confirms the head to tail linkage in the main chain. Similar studies were done for N-vinyl-2-pyrrolidone / methacrylonitrile (*V/N*) copolymers. The effect of the insertion of methyl group in the main chain is also discussed in this chapter.

Chapter four is devoted to the stereochemical and compositional assignments of the N-vinyl-2-pyrrolidone with glycidyl methacrylate (*V/G*) and methyl methacrylate (*V/M*) copolymers. The copolymer composition of the *V/G* copolymer was analyzed by ^{1}H NMR spectroscopy, whereas, for the *V/M* copolymer no separate signals were observed in ^{1}H NMR and ^{13}C{^{1}H} NMR spectra, therefore for these copolymers the copolymer composition was analyzed by the CHN elemental analysis. The reactivity ratios obtained from the KT and EVM methods for the N-vinyl-2-pyrrolidone / glycidyl methacrylate (*V/G*) copolymer are $r_V = 0.03 \pm 0.01$, $r_G = 5.05 \pm 0.84$ and $r_V = 0.02$ and $r_G = 4.72$, respectively. The methylene carbon resonance signals have been assigned up to the tetrad compositional and configurational sequences using 2D HSQC spectra. The methyl carbon resonances of *G* unit were assigned upto pentad compositional and configurational sequences. The geminal couplings obtained in the TOCSY spectra confirmed the presence of inequivalent protons of methylene group obtained in the HSQC spectra. The various CH/CH_2 couplings in the protons are also discussed in this chapter. Similar investigations were carried out for the N-vinyl-2-pyrrolidone / methyl methacrylate (*V/M*) copolymers. The comonomer reactivity ratios for *V/M* copolymer

determined by KT and EVM methods are $r_V = 0.02 \pm 0.01$, $r_M = 5.15 \pm 0.04$ and $r_V = 0.03$, $r_M = 5.05$, respectively. The effect of side group on the sequence distribution of the copolymer is also discussed in this chapter.

The **chapter five** is devoted to the microstructure of the N-vinyl-2-pyrrolidone with alkyl acrylates (alkyl = methyl, butyl). The copolymer composition of the N-vinyl-2-pyrrolidone / methyl acrylate (*V/M*) copolymer was determined by the ^{1}H NMR spectra, whereas for the N-vinyl-2-pyrrolidone / butyl acrylate (*V/B*) copolymer it was determined by the quantitative $^{13}C\{^1H\}$ NMR spectra. The reactivity ratios of the *V/M* copolymers, calculated from the KT and EVM methods are $r_V = 0.09 \pm 0.03$, $r_M = 0.41 \pm 0.09$ and $r_V = 0.09$, $r_M = 0.44$ respectively. By using DEPT-90 the methine resonances of *M* unit were assigned upto triad compositional and configurational sequences, which were confirmed by the crosspeaks obtained in 2D HSQC spectrum. The methine resonances of *V* unit were shown only upto triad compositional sequences. The β-CH_2 also shown to dyad configurational sequences. The presence of the inequivalent protons due to the meso configuration were confirmed by the geminal couplings in the 2D TOCSY NMR spectra. Similar experiments were carried out for the N-vinyl-2-pyrrolidone / butyl acrylate (*V/B*) copolymers.

The **sixth chapter** deals with the microstructure determination of the N-vinyl-2-pyrrolidone / vinyl acetate (*V/A*) copolymers. The copolymer composition of the *V/A* copolymer was determined from the quantitative $^{13}C\{^1H\}$ NMR spectra. The reactivity ratios of the *V/A* copolymers, calculated from the KT and EVM methods are $r_V = 2.86 \pm 0.16$, $r_A = 0.35 \pm 0.09$ and $r_V = 2.56$, $r_A = 0.33$, respectively. The carbonyl carbons of *V*- and *A*- centered resonances were used for determining the sequences in terms of the

distribution of *V*- and *A*- centered triads. The -CH of *A* unit in the *V/A* copolymer was assigned to triad compositional and configurational sequences. The overlapped signals were resolved along the proton axis in the 2D HSQC spectra. The methylene carbon resonances were assigned to tetrad compositional and configurational sequences. The proton NMR spectra of these copolymers were assigned with the help of 2D HSQC NMR experiments. All the crosspeaks in the TOCSY spectrum have been assigned to the couplings between the methine and methylene protons. The geminal couplings in the methylene protons were shown in 2D TOCSY spectrum.

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