MICROSTRUCTURE DETERMINATION OF GLYCIDYL -METHACRYLATE COPOLYMERS BY NMR SPECTROSCOPY

by

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DEDICATED

TO

MY PARENTS, BROTHER, SISTERS

CERTIFICATE

This is to certify that the thesis entitled, " **Microstructure Determination of Glycidyl methacrylate Copolymers by NMR Spectroscopy** ", being submitted by Mrs. Anil Yadav 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. Mrs. Anil Yadav 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 works embodied in this 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

Glycidyl methacrylate (GMA) based copolymers are of great industrial application due to the presence of reactive epoxide ring, which offers it an opportunity to enter into wide range of chemical reactions. One of the most promising approaches is the synthesis of new copolymers that can be used as macromolecular support and carrier for drugs. The GMA based copolymers have also been used in electronics as negative electron beam resists.

The physical and chemical properties of polymers/ copolymers are influenced fundamentally by the microstructure, which involves the sequence distribution and the stereochemical arrangements of various monomer units in the polymer chain. The information obtained from microstructure can further be used to synthesize the copolymer with the desired physico-chemical properties and to give information about the mechanism of copolymerization.

Keeping in view the significance of the determination of microstructure of polymers, this work was undertaken, with a purpose to develop the statistical and experimental basis for characterizing the structure of glycidyl methacrylate copolymers at molecular level. One- dimensional experiments are 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 this research work, we have tried to determine the compositional and configurational sequences of glycidyl methacrylate copolymers 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** describes the general introduction about the microstructure of the polymers and the review of the literature related to NMR of polymers. It also describes the use of one- and two-dimensional NMR spectroscopy for microstructure and sequence determination of polymers.

The **second chapter** describes the experimental procedures for the preparation of homopolymers and copolymers by methods such as bulk and solution polymerization using benzoyl peroxide (BPO) as an initiator. The experimental details of the determination of molecular weight by GPC method are also given. The chapter also includes the detailed description of all one and two-dimensional NMR experiments carried out throughout this research work.

The **third chapter** deals with the microstructure determination of the glycidyl methacrylate/ methyl acrylate (G/M) and glycidyl methacrylate/butyl acrylate (G/B) copolymers. The copolymers were prepared by solution polymerization using benzene as a solvent and BPO as an initiator. The copolymer composition was determined from ^1H NMR spectrum. The comonomer reactivity ratios were determined by both Kelen Tudos (KT) and non-linear least-square error in variables (EVM) methods using the copolymer composition data. These reactivity ratios for G/M copolymers are found to be r_G =4.03 ± 0.7, r_M = 0.45 ± 0.07 and r_G=4.6, r_M= 0.49, respectively while for G/B copolymers these values are found to be r_G = 2.81 ±0.53, r_B = 0.45 ± 0.085 and r_G= 2.77, r_B= 0.44, respectively. The DEPT 135 NMR and DEPT 90 NMR spectra were used to differentiate the resonance signals of the methine and methylene carbons in the copolymer. In both the G/M and the G/B copolymers, the α- methine group is overlapped with β-methylene group in the copolymer, while the methyl group of B- unit in G/B copolymer is

overlapped with α-CH_3 group of G- unit along the carbon axis and with β-methylene group along proton axis. The 2D HSQC NMR technique was used to resolve these overlapped groups. The β-methylene group is assigned to dyad and tetrad compositional sequences with the help of HSQC NMR spectrum. The assignments done for β-methylene group using HSQC NMR spectrum were further confirmed by observing the cross peaks due to vicinal coupling of methine proton with methylene protons in various dyads and geminal coupling of inequivalent methylene protons in 2D TOCSY NMR spectrum.

Chapter four describes the stereochemical and compositional assignments of the glycidyl methacrylate/vinyl acetate (G/V) and glycidyl methacrylate/vinylidene chloride (G/C) copolymers. The copolymer composition of the G/V copolymers was analyzed from ^{1}H NMR spectrum, whereas for the G/C copolymers it was analyzed from the quantitative ^{13}C NMR spectrum. The reactivity ratios obtained from the KT and EVM methods for the G/V copolymer are $r_G = 37.4 \pm 12.0$, $r_V = 0.036 \pm 0.019$ and $r_G = 35.2$, $r_V = 0.03$ respectively while for G/C copolymers these values are $r_G = 2.55 \pm 0.56$, $r_c = .26 \pm 0.06$ and $r_G = 2.7$, $r_c = 0.27$, respectively. In $^{13}C\{^1H\}$ NMR of the G/V copolymer, the methyl group of V- unit is overlapped with α-methyl group of G- unit, however, the assignments could still be done to higher compositional/ configurational levels by observing the change in intensity of the resonance signals with the change in the copolymer composition. The 2D HSQC NMR spectrum was used to confirm these assignments and to assign the β-methylene carbon resonances to various compositional sequences. Similar microstructural investigations were carried out for the glycidyl methacrylate/vinylidene chloride (G/C) copolymer. In G/C copolymer, the carbonyl

carbon and α-methyl group carbon of G- unit and quaternary carbon of C- is unit assigned to triad levels in $^{13}C\{^{1}H\}$ NMR spectrum. The β-methylene carbon resonances are very well resolved and assigned to tetrad sequences using 2D HSQC NMR spectrum. The 2D TOCSY NMR spectrum was used to confirm the assignments done for β-methylene protons in 2D HSQC NMR spectrum.

The microstructure of the glycidyl methacrylate/ styrene (G/S) and glycidyl methacrylate/α-methyl styrene (G/M) copolymers are presented in **chapter five**. Since the proton NMR spectrum of G/S and G/M copolymers is very broad and overlapped, the copolymer composition of the G/S and G/M copolymers was determined from the quantitative ^{13}C NMR spectrum. The reactivity ratios of the G/S copolymer, calculated from the KT and EVM methods are $r_G = 0.56 \pm 0.1$, $r_S = 0.44 \pm 0.07$ and $r_G = 0.60$, $r_S = 0.48$ respectively, while for G/M these values are found to be $r_G = 1{:}12 \pm 0.2$, $r_M = 0.05 \pm 0.02$ and $r_G = 1.29$, $r_M = 0.07$, respectively. The α-methine carbon resonances in G/S copolymer are assigned to triad sequences; methyl carbon resonances to pentad sequences and the methylene carbon resonances are assigned to tetrad sequences with the help of 2D HSQC NMR spectrum. The aromatic methine proton region of styrene is assigned to pentad level using the 2D TOCSY NMR spectrum. Similar studies were carried for glycidyl methacrylate/α-methyl styrene (G/M) copolymers.

The microstructure of the glycidyl methacrylate/ methacrylonitrile (G/M) copolymers is reported in **chapter six.** The copolymer composition of the G/M copolymers was determined from the quantitative ^{13}C NMR spectrum. The reactivity ratios of the G/M copolymers, calculated from the KT and EVM methods are $r_G = 1.14 \pm 0.1$, $r_M = 0.76 \pm 0.06$ and $r_G = 1.12$, $r_M = 0.75$ respectively. The carbonyl and nitrile carbon resonances are

assigned to triad sequences, α-methyl carbon resonances to pentad compositional and configurational sequence and the methylene carbon resonances are assigned to dyad sequence with the help of 2D HSQC NMR spectrum. The inequivalent methylene protons give cross peak due to geminal coupling in 2D TOCSY NMR spectrum.

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