CHARACTERIZATION OF ISOBORNYL ACRYLATE AND METHACRYLATE COPOLYMERS BY NMR SPECTROSCOPY

by

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Certificate

This is to certify that the thesis entitled, "CHARACTERIZATION OF ISOBORNYL ACRYLATE AND METHACRYLATE COPOLYMERS BY NMR SPECTROSCOPY", being submitted by **Ms. Deepika Khandelwal** to Indian Institute of Technology, Delhi, for the award of the Degree of Doctor of Philosophy, is a record of bonafied research work carried out by her. She has worked under our supervision and guidance and has fulfilled all the requirements for the submission of a Ph.D. thesis, which to our knowledge has reached the requisite standard and is worthy of consideration for the award of the Ph.D. degree.

The results contained in this dissertation have 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

The copolymers comprising of isobornyl acrylate and isobornyl methacrylate are materials of significant commercial importance and have attracted much attention in academics and industry. These copolymers have specific applications in adhesive, coating industries, cosmetics and drug delivery systems etc. These polymers, which are used to make the ‘‘construction material’’ for microfluidic devices has the qualities of low viscosity during injection, optical patterning and good resolution for exposure, transparency for visual observation and low shrinkage during polymerization. These polymers do not react with common solvents, such as methanol, ethanol or isopropanol.

Free radical polymerization is widely used because of mild reaction conditions, and tolerance to impurities. The advent of Controlled Radical Polymerization (CRP) produces well-defined polymers with predicted molecular weight, narrow molecular weight distributions and high degree of end functionalization. This offers a great advantage over other methods of polymerization in designing novel polymeric materials with specific structures and controlled molecular weight. Atom transfer radical polymerization (ATRP) is a living radical polymerization based on a reversible exchange between growing radicals and dormant species. This dynamic equilibrium keeps control over the termination as well as side reactions and leading to uniform growth of polymer chains throughout the polymerization process. In ATRP, variation in relative concentration of monomers is reflected along all the chains and the distribution or arrangement of monomer units influences the physical properties of polymers to a great extent.

High-resolution NMR spectroscopy has proven to be one of the most informative technique for the microstructure analysis. NMR spectroscopy plays an important role in monitoring the extent of reaction, checking the purity of polymer samples along with their identification. Various 1D and 2D NMR techniques help in detection of end groups and the tacticity of synthesized polymers. NMR studies are often motivated by a desire to understand structure-property relationships at the molecular level. Chemical shifts are sensitive to configurational and compositional sequences; thus, different microstructures can be resolved by NMR spectrum. Quantitative estimation of monomers in copolymers can be carried out by various NMR techniques like ^{1}H and quantitative $^{13}C\{^{1}H\}$ NMR spectra. It is often observed that polymers with similar monomer compositions have different mechanical, thermal, optical or electrical properties as a consequence of differences in microstructure. Due to the complexity of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of copolymers, complete assignments is a difficult task. Nevertheless, the high information content of fully interpreted spectra, it remains an important area to investigate. 1D NMR techniques especially DEPT NMR has been used to distinguish various methyl, methylene and methine signals. Further, 2D NMR methods have been extensively used in the unambiguous assignments of ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of polymers. 2D NMR techniques involve a study of ^{1}H-^{13}C correlation by Heteronuclear Single Quantum Coherence (HSQC), proton-proton coupling by Total Correlation Spectroscopy (TOCSY) and long range coupling between heteroatoms by Heteronuclear Multiple Bond Correlation (HMBC) NMR experiments. These studies help in unambiguous stereochemical and compositional assignments of ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of the polymers.

Monomer sequence distributions have a direct bearing on the chemical and physical properties of copolymers. Keeping in view the importance of polymer microstructure, the present study is undertaken with a purpose to understand the experimental basis for characterizing the structure of copolymer chains at the molecular level.

The present thesis is an attempt to undertake a systematic study on the synthesis of isobornyl acrylate and methacrylate homo and copolymers and their characterization by different NMR techniques. The thesis consists of six chapters.

Chapter I consists of literature survey on isobornyl acrylate and isobornyl methacrylate containing copolymers, synthesized by free radical polymerization and by ATRP. This chapter also deals with the literature survey on current advances in the field of "ATRP" and "NMR of Polymers". A general introduction to ATRP with emphasis on its mechanism and kinetic studies is covered. The use of various initiators and catalyst systems for controlled polymerization of a wide range of monomers under ATRP conditions has been reviewed. The importance of NMR spectroscopy in analyzing the sequence distribution of polymers and their characterization is also incorporated in chapter I. The approach applied in the current research, and its contribution to the field of NMR and polymers is also highlighted. A general introduction to the polymer microstructure with special emphasis on the sequence distribution is included. The theoretical basis and experimental details about optimization of the reactivity ratios from infeed/outfeed fractions are also given.

Chapter II includes the experimental details for the preparation of homopolymers and copolymers by Free Radical Polymerization and ATRP. Experimental details of Molecular weight determination by GPC are also given. The compositional aspects as determined by ^{1}H NMR and quantitative $^{13}C\{^{1}H\}$ NMR spectra have been explained. The experimental details for 1D (^{1}H, $^{13}C\{^{1}H\}$ and DEPT) and 2D (HSQC, TOCSY and HMBC) NMR experiments are incorporated. The theoretical basis and experimental details about optimization of reactivity ratios from infeed/outfeed fractions using the least square methodology are also covered.

Chapter III deals with the synthesis and characterization of homopolymers of isobornyl acrylate and isobornyl methacrylate using copper based ATRP. The configurational sequence of poly(isobornyl acrylate) (PiBA) and poly(isobornyl methacrylate) (PiBMA) is determined with the help of 1D and 2D NMR techniques. The methine carbon of PiBA is assigned upto triad level of configurational sequences. The stereoregularity (tacticity) of PiBA has been calculated using methine carbon resonance of quantitative $^{13}C\{^{1}H\}$ NMR spectrum and the results show nearly random structure i.e. mm = 20%, mr = 53% and rr = 27%. The α-methyl and carbonyl carbons of PiBMA is assigned up to triad level of configurational sequences in $^{13}C\{^{1}H\}$ NMR spectrum, whereas β-methylene carbon resonances are assigned upto diad level of configurational sequences. The stereo regularity of PiBMA (mm = 4%, mr = 42%, and rr = 54%) indicates the formation of random polymer.

Chapter IV includes the sequence determination of isobornyl acrylate/methyl methacrylate (B/M) and isobornyl methacrylate/methyl acrylate

(I/M) copolymers, synthesized by ATRP. The molar ratios of ATRP components for copolymerization are taken as [Monomer]:[MBP]:[CuBr]:[PMDETA] = 100:1:1:1. Variation of feed composition led to copolymers with different compositions. Molecular weights of the copolymers have been determined by Gel Permeation Chromatography (GPC). The composition of copolymers has been determined from ^{1}H NMR spectra. The copolymer composition data has been used to determine the reactivity ratios by Kelen-Tudos (KT) and nonlinear error in variables methods (EVM). The reactivity ratios of monomers in B/M copolymer determined from a linear KT method and EVM are: r_B = 0.41±0.11, r_M = 1.11±0.33 and r_B = 0.52, r_M = 1.31 and for I/M copolymer are r_I = 1.25±0.10, r_M = 0.84±0.08 and r_I = 1.20, r_M = 0.82 respectively. ^{13}C {^{1}H} NMR spectra of these copolymers show that the methylene and methine signals of the main chain are compositional and configurational sensitive and highly overlapped. Even DEPT spectra were not able to assign the complex and overlapped signals. The assignments of various resonance signals have been made with the help of 2D HSQC, TOCSY and HMBC NMR experiments. 2D HSQC was used to simplify the complex ^{1}H NMR spectra of the copolymers. The methylene carbon resonances of B and M units have been assigned upto tetrad level of compositional and configurational sequences. 2D TOCSY experiments have been used to make unambiguous assignments from various coupling between the protons of copolymers. The vicinal couplings between methine protons in B centered triads with the methylene protons in BB and BM centered tetrad of B/M copolymer have been assigned by TOCSY spectra of different copolymer composition. The α-methyl and carbonyl carbons of these copolymers are assigned to triad level of configurational and compositional sequences. The long

range interactions of quaternary and carbonyl carbons with methyl, methylene, methine and methoxy protons are observed in 2D HMBC spectra.

Chapter V deals with NMR studies of isobornyl acrylate/methacrylonitrile (B/N) and isobornyl methacrylate/acrylonitrile (I/A) copolymers. These copolymers have been synthesized by free radical polymerization using AIBN as initiator. The compositions of each copolymer are determined with the help of quantitative $^{13}C\{^{1}H\}$ NMR spectra. The reactivity ratios determined from a linear KT Method and EVM in B/N copolymer, are $r_B = 0.66\pm0.11$, $r_N = 1.54\pm0.22$ and $r_B = 0.74$, $r_N = 1.65$ respectively, whereas for I/A copolymers are $r_I = 1.63\pm0.15$, $r_A = 0.61\pm0.07$ and $r_I = 1.57$, $r_A = 0.60$ respectively. One to one correlation between carbon and proton in 2D HSQC spectra and cross-correlation peaks between non-equivalent protons in 2D TOCSY spectra have enabled to assign the methylene, methine and α-methyl protons resonance signals in the overlapping ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra unequivocally. Further, compositional assignments in the complex and overlapping signals of carbonyl carbon in $^{13}C\{^{1}H\}$ NMR spectra are confirmed with the help of 2D HMBC spectra. The nitrile, methine and OCH carbons of B/N copolymer are assigned upto triad level of compositional sequences. The long range interactions of quaternary, nitrile and carbonyl carbons with methyl, methylene and methine protons are assigned by 2D HMBC spectrum.

Chapter VI illustrates the microstructure determination of styrene copolymers with isobornyl acrylate and isobornyl methacrylate synthesized by ATRP. The composition of the copolymers are analysed by ^{1}H NMR spectra. The

monomer reactivity ratio determined by KT method and EVM for B/S copolymer are $r_B = 0.41\pm0.08$, $r_S = 0.92\pm0.13$ and $r_B = 0.41$, $r_S = 0.93$ and for I/S copolymer are $r_I = 0.39\pm0.09$, $r_S = 0.44\pm0.08$ and $r_I = 0.42$, $r_S = 0.47$. The stereo sequence assignments of various resonance signals in ^1H and $^{13}C\{^1H\}$ NMR spectra have been made with the help of 2D HSQC and TOCSY experiments. The α-methyl and carbonyl carbon resonances of both the copolymers are assigned upto triad compositional and configurational sequences, while methylene carbon resonances are assigned upto tetrad level of compositional and configurational sequences. The methine and quaternary carbons of styrene are assigned upto triad level of compositional sequences whereas α-methyl carbon of I unit and methine carbon of S unit in I/S copolymer are assigned upto triad level of compositional and configurational sequences. The long range interactions of different aromatic carbons are completely assigned in 2D HMBC spectrum.

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