# SYNTHESIS AND CHARACTERIZATION OF VINYL COPOLYMERS AND TERPOLYMERS BY NMR SPECTROSCOPY

**ASHOK KUMAR GOYAL**


**DEPARTMENT OF CHEMISTRY**

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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*by*

**ASHOK KUMAR GOYAL**
DEPARTMENT OF CHEMISTRY

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*Dedicated*

*With Love*

*To*

**My Father**

***WHO COULD NOT SEE ME HERE IN THIS DAY...***

# Certificate

This is to certify that the thesis entitled, "SYNTHESIS AND CHARACTERIZATION OF VINYL COPOLYMERS AND TERPOLYMERS BY NMR SPECTROSCOPY", being submitted by **Mr. Ashok Kumar Goyal** 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 him. Mr. Ashok Kumar Goyal 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 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.

(A. S. Brar)
Thesis Supervisor
Professor,
Department of Chemistry
Indian Institute of Technology,
Technology,
Delhi, New Delhi-110 016
INDIA

(Ravi Shankar)
Thesis Co-Supervisor
Professor,
Department of Chemistry
Indian Institute of
Delhi,New Delhi-110 016
INDIA

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**(Ashok Kumar Goyal)**

## ABSTRACT

Vinyl copolymers and terpolymers, being the materials of significant commercial importance, have attracted much attention in academics and industry. There is a growing interest in the enhancement of the chemical and physical properties of these polymers. Terpolymerization is a promising technique that provides a convenient method to synthesize new polymeric materials with wide range of properties. The interest in multifunctional synthetic polymers or copolymers is steadily increasing as macromolecular catalysts, drugs or anti-static agents etc.

Free radical polymerization is widely used for the synthesis of these polymeric materials because of the availability of a wide range of readily polymerizable monomers, 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 one of the versatile techniques of Controlled Radical Polymerization (CRP) which gives finer control over molecular weight and polymer architecture due to its tolerance to a wide range of monomers and solvents of different polarity. In ATRP, the variation in relative concentration of monomers is reflected along all the chains, and the distribution of monomer units influences the physical properties of polymers to a great extent. Hence, the knowledge about the composition and distribution of

monomer units along the macromolecular chains is important to correlate the structure-property relationship. The basis of ATRP is the reversible transfer of a radically transferable atom, typically a halogen atom, from a monomeric or polymeric alkyl (pseudo) halide to a transition metal complex in a lower oxidation state, forming an organic radical and a transition metal complex in a higher oxidation state

High-resolution NMR spectroscopy has proven to be one of the most informative techniques for the microstructure determination of polymers. NMR spectroscopy plays an important role in monitoring the extent of reaction, checking the purity of polymer samples along with their identification. Chemical shifts are sensitive to configurational and compositional sequences; thus, different microstructures can be resolved in the NMR spectrum. It is often observed that the macroscopic properties of polymers are critically dependent on the microstructure. Various 2D NMR techniques in conjugation with 1D NMR techniques helps in the detection of end groups and in determining the tacticity of polymers synthesized by ATRP and thus helps in the understanding of polymerization mechanism involved.

The thesis consists of six chapters. ***Chapter 1*** contains the introduction to various types of polymerization, significance of controlled radical polymerization and the importance of ATRP. The literature survey on the current advances in the field of "Atom Transfer Radical Polymerization" and "NMR of Polymers" has been reviewed. A general introduction to ATRP regarding its mechanism and kinetic studies is covered. The use of various initiators and catalyst systems for the controlled polymerization of 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. The approach applied for the current research, and its contribution to the field of NMR and polymers is also highlighted. The theoretical basis and experimental details about the optimization of the reactivity ratios from the infeed/outfeed fractions are also given.

***Chapter 2*** contains the experimental details for the preparation of homopolymers, copolymers and terpolymers. It is also includes the optimization of polymerization reactions by ATRP using different initiators and catalyst systems. Experimental details of the molecular weight determination by GPC are given. The experimental details for the 1D ($^{1}H$, $^{13}C\{^{1}H\}$, DEPT) and 2D (heteronuclear single quantum correlation (HSQC), total correlated spectroscopy (TOCSY), and heteronuclear multiple bond correlation (HMBC)) NMR experiments are incorporated. The theoretical basis and experimental details about the optimization of the reactivity ratios from the infeed/outfeed fractions using the least square methods are also given.

***Chapter 3*** deals with the synthesis and characterization of Glycidyl methacrylate (G) and Styrene (S) copolymers using copper based ATRP. High monomer conversions within reasonable time were desired while maintaining control over molecular weight distribution. The effect of various reaction parameters on the rate of polymerization, variation in temperature, type of initiator, ligand and solvent used for ATRP were examined, to achieve controlled polymerizations. A series of G/S copolymers with varying infeed molar ratios were synthesized in bulk at 60°C temperature using CuBr/PMDETA catalyst and

EBiB as initiator with optimized molar ratio $[Monomer]_0$: $[EBiB]_0$: $[CuBr]_0$: $[PMDETA]_0$ = 100: 1: 0.5: 0.5.

The controlled nature of polymerization was demonstrated by linear evolution of molecular weights with conversion while maintaining low polydispersities [$1.1<(M_w/M_n)<1.4$]. The living nature of polymerization was further confirmed by performing the kinetic study. The copolymer composition obtained from $^1$H NMR spectra were utilized to determine the monomer reactivity ratios ($r_G = 0.73$ and $r_S = 0.42$) involved in ATRP.

***Chapter 4*** includes the sequence determination of the acrylonitrile/methyl methacrylate/methyl acrylate(A/B/M) terpolymers. These terpolymers have been synthesized by ATRP. The molar ratios of ATRP components for terpolymerization are taken as [Monomer]:[MBP]:[CuBr]:[dNbpy] = 100:1:0.5:0.5. Variation of feed composition led to terpolymers with different compositions. Molecular weights of the terpolymers have been determined by Gel Permeation Chromatography (GPC). Percentage conversion was determined gravimetrically. The composition of terpolymers has been determined from quantitative $^{13}C\{^1H\}$ NMR and found in good agreement with those of theoretical compositions calculated by Alfrey-Goldfinger's equation.

The microstructure has been studied in terms of the distribution of A-, B- and M- centered triad sequences from $^{13}C\{^1H\}$ NMR spectra of the terpolymers. With the help of $^{13}C\{^1H\}$ and DEPT NMR, the distinction between various carbon resonance signals (methyl, methylene, methine and quaternary carbons) is achieved. $^{13}C\{^1H\}$ NMR spectra of these terpolymers show that the NMR signals of methylene and methine carbon of the main chain and α-methyl carbon are

compositional and configurational sensitive and highly overlapped. The overlapping and broad signals of terpolymers are assigned completely to various compositional and configurational sequences by correlating 1D ($^1$H, $^{13}$C{$^1$H}, DEPT) and 2D (HSQC, TOCSY, HMBC) NMR spectral data. The configurational and compositional sensitivity of carbonyl carbon regions was investigated through the analysis of long range couplings between carbon and protons with the help of 2D HMBC NMR experiments. The completely assigned $^1$H NMR spectra are utilized to make assignments in 2D HMBC spectra, which further verify the assignments made using 2D HSQC and TOCSY spectral analysis.

***Chapter 5*** deals with the NMR studies of the methyl acrylate/vinyl acetate/N-vinyl carbazole (M/V/C) terpolymers. These terpolymers were synthesized by free radical polymerization using toluene as solvent. Molecular weight distributions were determined by GPC. The composition of the terpolymer was determined by the help of quantitative $^{13}$C{$^1$H} NMR. The carbonyl carbon resonances were found to be compositionally sensitive. Methine carbon resonances of the methyl acrylate (A), vinyl acetate (V) and N-vinyl carbazole (C) units were assigned up to triad level of compositional sensitivity and methylene carbon resonances were assigned upto diad configyrational sensitivity. One to one correlation between carbon and proton in the 2D HSQC and cross-correlation peaks between nonequivalent protons in the 2D TOCSY enabled to assign the methylene, methine and α-methyl proton 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 the $^{13}$C{$^1$H} NMR spectra were confirmed with the help of 2D HMBC.

***Chapter 6*** illustrates the microstructure determination of 2-hydroxy ethyl methacrylate (H) copolymers with mathacrylonitrile (N) and 2-Vinyl pyridine (P). These copolymers were synthesized by free radical bulk polymerization. The compositions of the copolymers were analysed by $^{1}H$ NMR. The monomer reactivity ratios optimized by two Errors in variable method (EVM) are found as: $r_H = 0.52$, $r_N = 0.66$ for H/N copolymers while $r_H = 0.55$, $r_P = 1.06$ are found for H/P copolymers. The stereo sequence assignments of various resonance signals in $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were made with the help of 2D HSQC and TOCSY experiments. The α-methyl and carbonyl carbon resonances of both the copolymers were assigned upto triad compositional and configurational sequences while methylene carbon resonances were assigned upto diad configurational sequences.

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