NMR AND MÖSSBAUER STUDIES OF SOME VINYL COPOLYMERS

by

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Dedicated to
my Parents

CERTIFICATE

This is to certify that the thesis entitled, "NMR AND MÖSSBAUER STUDIES OF SOME VINYL COPOLYMERS", being submitted by Ms. Sunita 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 her. Ms. Sunita has worked under my supervision and guidance and has fulfilled all the requirements for the submission of this thesis which to our 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.

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ABSTRACT

Detailed understanding of the microstructure of synthetic vinyl copolymers is of both fundamental and practical significance. The knowledge of copolymer composition and sequence distribution is an important step in the evaluation of their utility. Keeping in view the importance of polymer microstructure, a work was undertaken with a purpose to develop the theoretical and experimental basis for characterizing the structure of copolymer chains at the molecular level. The thesis describes the preparation and characterization of four series of copolymers of acrylonitrile - alkyl acrylate, styrene - alkyl acrylate, acrylic acid - alkyl acrylate and vinyl acetate copolymers. These copolymers were doped with ferric chloride and studied using Mössbauer spectroscopy.

The thesis consists of six chapters. The first introductory chapter briefly summarizes some aspects of the copolymer microstructure and statistical models. It also encompasses brief discussion on the basic principle of Mössbauer spectroscopy and the nature of information which can be obtained for iron containing copolymers. Some land marks reached in earlier studies have been high lighted.

The chapter-II describes the experimental procedures for the preparation of homopolymers and copolymers, which are mainly prepared by free radical bulk polymerization. The above

copolymers were also prepared by adding ferric chloride during the course of polymerization. The molecular weights of the copolymers were determined by gel permeation chromatography (GPC) and viscometry. ^{1}H - NMR spectra, volumetric and C, H and N analyses were used to determine the copolymer composition. Differential scanning calorimetry (DSC) was used to measure Tg of different copolymers. $^{13}C\{^{1}H\}$-NMR spectra were recorded and used to describe the microstructure of copolymers. Mössbauer studies were carried out in order to understand the nature and environments of iron nucleus in the copolymers containing ferric chloride. Thermal gravimetric analysis (TGA) was carried out to study the thermal stability of copolymers. Infrared spectroscopy has been used for the identification of species formed during the thermal decomposition of copolymers.

Comonomer reactivity ratios were determined by nonlinear least square error-in-variables method (EVM) with the use of computer program written by O'Driscoll et al. The comonomer sequence distribution and all the calculations regarding the fractional area measurements in NMR and Mössbauer spectra were performed using a deconvolution computer program on ICL-3960 main frame computer.

The first part of the chapter - III explains the copolymerization behaviour of acrylonitrile (A) - methyl acrylate (M), acrylonitrile (A) - ethyl acrylate (E), acrylonitrile (A) - butyl acrylate (B) copolymers. Copolymer composition was

determined by elemental analyses and comonomer reactivity ratios were obtained using EVM program. The value of reactivity ratios obtained from EVM program are $r_A = 0.56 \pm 0.03$, $r_M = 0.51 \pm 0.02$; $r_A = 0.92 \pm 0.07$, $r_E = 1.20 \pm 0.02$ and $r_A = 0.65 \pm 0.04$, $r_B = 0.84 \pm 0.02$. $^{13}C\{^1H\}$-NMR spectra have been analysed in order to determine triad comonomer sequence distribution. For A/M copolymer, the carbonyl carbon and nitrile carbon resonance signals around δ 174.0 and 120.0 ppm split into three main groups and are assigned to six possible triad sequences with the help of variable composition carbon - 13 NMR spectra. Terminal and penultimate model reactivity ratios have been calculated using the observed monomer triad sequence distribution obtained from $^{13}C\{^1H\}$-NMR spectra. The triad sequence distribution was used to calculate diad concentrations, conditional probability parameters, number - average sequence lengths and run number in the copolymers. The observed triad sequence concentrations determined from $^{13}C\{^1H\}$-NMR spectra agreed well with those calculated from reactivity ratios. Glass transition temperature (Tg) of various copolymers determined from DSC gave good agreement with those obtained from Tg - diad relationships.

Second part of chapter-III, includes the results of Mössbauer studies of above copolymers doped with ferric chloride. No changes in oxidation state of iron have been observed during the copolymerization. TGA studies shows that the addition of ferric chloride stabilized the copolymers by 20-25°C. Mössbauer studies

of copolymers heated at 300°C, 400°C and 500°C for 15 minutes showed that during the thermal degradation, Fe^{3+} species reduced to Fe^{2+} and finally α-Fe_2O_3 is formed, which was confirmed by IR spectroscopy. Oxidation - reduction, and substitution reactions have been attributed to the increased thermal stability of doped copolymers.

The first part of chapter-IV, includes the details on copolymerization of styrene (S)-methyl acrylate (M), styrene (S)-ethyl acrylate (E), styrene (S) - butyl acrylate (B) copolymers. Copolymer composition was determined from ^{1}H-NMR spectra. Comonomer reactivity ratios have been obtained from various methods, the reactivity ratios being $r_S=1.33\pm0.26$, $r_M=0.20\pm0.03$; $r_S=1.16\pm0.20$, $r_E=0.22\pm0.02$ and $r_S=1.21\pm0.21$, $r_B=0.17\pm0.03$. The carbonyl carbon signals around δ 175.0 ppm and quaternary carbon resonance signals around δ 144.0 ppm in $^{13}C\{^1H\}$-NMR spectra have been attributed to various M- and S- centered triad sequences in S/M copolymers. Coisotacticity parameter (σ) have been calculated from NMR spectroscopy using -oxymethylene resonance signal in ^{1}H-NMR spectra. The value of coisotactic parameter (σ) for styrene - alkyl acrylate copolymers is $\approx$ 0.85, indicates the tendency toward random copolymerization. Glass transition temperature of various copolymers was calculated from NMR spectra.

Second part of chapter - IV, includes the results of Mössbauer studies of above copolymers doped with ferric chloride which showed no reduction of Fe^{3+} species during the polymerization process. Thermal stability of copolymers increased by ≈30°C. Mössbauer spectra of copolymers heated at different temperature revealed the presence of more asymmetric environment around Fe(III) and the reduction to Fe(II) was also observed. Heating of the doped copolymers at 500°C resulted in the formation of α-Fe_2O_3.

The first part of chapter- V, includes the details on the copolymerization behaviour of acrylic acid (A)-methyl acrylate (M), acrylic acid (A) - ethyl acrylate (E) and acrylic acid (A)-butyl acrylate (B) copolymers. Copolymer composition was determined from volumetric analyses. The values of reactivity ratios obtained from EVM program are $r_A = 0.45 \pm 0.07$, $r_M = 0.66 \pm 0.03$; $r_A = 0.58 \pm 0.08$, $r_E = 0.83 \pm 0.04$ and $r_A = 0.39 \pm 0.07$, $r_B = 1.08 \pm 0.06$. All the resonance signals in $^{13}C\{^1H\}$- NMR spectra of acrylic acid - alkyl acrylate copolymers are insensitive to various monomer placements so the compositional sequence distribution is not calculated in these copolymers. The triad/diad sequences distribution is mainly obtained from Alfrey - Mayo model.

Second part of chapter-V, contains the results of Mössbauer studies of above copolymers doped with ferric chloride. The addition of ferric chloride does not change the thermal stability

of these copolymers to much extent. At higher temperature reduction of Fe^{3+} to Fe^{2+} species was observed. IR and Mössbauer studies of the doped copolymers heated at 500°C showed the presence of α-Fe_2O_3.

The purpose of the work described in chapter - VI is to prepare and characterize the copolymers of vinyl acetate (V) - acrylonitrile (A) and vinyl acetate (V) - acrylic acid (A') The copolymer composition for vinyl acetate - acrylonitrile copolymers was determined by elemental analyses while for vinyl acetate-acrylic acid was determined by volumetric titration. The values of reactivity ratios obtained from EVM computer program are $r_V = 0.016 \pm 0.006$, $r_A = 5.95 \pm 0.93$ and $r_V = 0.042 \pm 0.006$, $r_{A'} = 3.07 \pm 0.29$. Terminal and penultimate reactivity ratios have been determined from $^{13}C\{^1H\}$-NMR spectra. Triad sequence distribution was used to calculate the diad compositions, probability parameters, number - average sequence lengths and comonomer mole fractions in the copolymers. The observed triad sequence concentrations determined from $^{13}C\{^1H\}$-NMR were found to be in good agreement with those calculated from reactivity ratios using Harwood program. Mössbauer studies were not carried out in vinyl acetate copolymers, because ferric chloride undergoes reaction with vinyl acetate monomer which inhibit the polymerization process.

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CHAPTER - II Experimental Details

CHAPTER-III NMR and Mössbauer Studies of Acrylonitrile - Alkyl Acrylate Copolymers

CHAPTER-IV NMR and Mössbauer Studies of Styrene-Alkyl Acrylate Copolymers