NMR AND MÖSSBAUER STUDIES OF COPOLYMERS

by

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dedicated to ..
My Mother

CERTIFICATE

This is to certify that the thesie entitled, "NMR AND MÖSSBAUER STUDIES OF COPOLYMERS", being submitted by Mr. Gurpreet Singh Kapur to the Indian Institute of Technology, Delhi, for the award of Degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Gurpreet Singh Kapur has worked under my supervision and fulfilled all the formalities as required under statutes before the submission of a Ph.D. thesis. This thesis has reached the requisite standard and is worthy of consideration for the award of 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.

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ABSTRACT

Monomer sequence distributions have a direct bearing on the chemical and physical properties of copolymers and a knowledge of the copolymer composition and microstructure 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 understand the theoretical and experimental basis for characterizing the structure of copolymer chains at the molecular level. The work described in this thesis comprised of preparation and characterisation of three series of copolymers of alkyl methacrylate / alkyl methacrylate, acrylonitrile / alkyl methacrylate, and vinyl acetate / alkyl methacrylate by nuclear magnetic resonance (NMR) spectroscopy. These copolymers were doped with ferric chloride and studied using Mössbauer spectroscopy.

The thesis consists of five chapters. The first introductory chapter briefly summarizes some aspects of copolymer microstructure and statistics. It also encompasses brief discussion on the basic principle of Mossbauer spectroscopy and the kind of information which can be obtained for iron containing homo/co polymers. Some land marks reached in earlier studies have been highlighted.

The chapter-II, describes the experimental procedures for the preparation of homopolymers and copolymers, which is mainly the free radical bulk polymerization except for the vinyl acetate copolymer series which were prepared by free radical initiated emulsion polymerization using a semicontinuous batch process. The above copolymer samples were also prepared by adding anhydrous ferric chloride during the course of polymerization. The molecular weights of the copolymers were determined by gel permeation chromatography and viscometry. ^{1}H-NMR spectra and C,H, and N analysis were used to obtain the copolymer composition wherever possible. ^{13}C[^{1}H]-NMR spectra were recorded and used to completely discern the microstructure of the copolymers. Mössbauer investigations 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 the samples. Infrared spectroscopy has been used for the identification of species formed during the thermal decomposition of copolymers.

Comonomer reactivity ratios and the theoretical comonomer sequence distributions were obtained by using various computer programs written in FORTRAN on PC-AT. All the calculations regarding the fractional area measurements in NMR and Mössbauer spectra were performed using a deconvolution computer program on ICL-2960 main frame computer.

The first part of the chapter III explains the copolymerization behaviour of methyl methacrylate / ethyl methacrylate(M/E), ethyl methacrylate/nbutyl methacrylate (E/B), and methyl methacrylate/nbutyl methacrylate (M/B) copolymers. Copolymer composition was determined by ^{1}H-NMR spectroscopy and comonomer reactivity ratios hitherto unestablished have been found to have the values: r_M=1.04, r_E=0.98; r_E=1.27, r_B=1.00; and r_M=0.96, r_B=1.04. ^{13}C[^{1}H]-NMR spectra have been analyzed in order to determine triad comonomer sequence distribution. The carbonyl carbon resonance δ177 (ppm downfield TMS) multiplicity has been attributed to various monomer centered triad sequences in M/B, M/E copolymers and to only configurational sequences in E/B copolymers. Triad sequence distributions have obtained over whole range of feed in monomer concentration. Harwood's computer program was used for estimating sequence distribution up to pentad for these copolymer systems.

Second part of the chapter III contains results of Mössbauer studies of above copolymers doped with ferric chloride. No changes in the oxidation state of iron have been observed during the polymerization. Thermal stability of these doped copolymers increased by ≈50°C after the inclusion of ferric chloride. Mössbauer spectra of the doped copolymers heated at different temperatures revealed the presence of more asymmetric environments around Fe^{3+} and in certain cases its reduction to Fe^{2+} was observed. The oxidation-reduction phenomenon was found to be more pronounced in those copolymers where ethyl methacrylate was one of the comonomer. Heating the doped polymers at 500°C resulted in the formation of α-Fe_2O_3. Oxidation-reduction, and substitution reactions have been attributed to the increased thermal stability of doped copolymers.

The first part of chapter IV, includes details on the copolymerization of acrylonitrile/methyl methacrylate (A/M), acrylonitrile/ethyl methacrylate (A/E), and acrylonitrile/nbutyl methacrylate (A/B) copolymers. Comonomer reactivity ratios have been obtained by various methods, the reactivity ratio values being $r_A = 0.21$, $r_M = 1.42$; $r_A = 0.18$, $r_E = 1.41$; and $r_A = 0.15$, $r_B = 0.93$, and are in good agreement with those reported in the literature. Both compositional and configurational effects have been observed in the $^{13}C[^1H]$-NMR spectra of these copolymers. Carbonyl resonance at δ176 ppm and nitrile resonance at δ120 ppm are each split into three main groups and are assigned to the six possible triad sequences with the help of variable composition carbon-13 NMR. Within a group further assignments have been made to various configurational arrangements. Penultimate group effect was found to be operative in all the cases, and the penultimate reactivity ratios obtained are in good agreement with the reported values. The configurational probabilities calculated from ^{13}C-NMR were indicative of random cotactic placements. A good agreement between the expected values of compositional and configurational sequence distribution and those obtained from ^{13}C-NMR spectroscopy was obtained.

Second part of chapter IV includes results of the Mössbauer studies of the above copolymers doped with ferric chloride which showed no reduction of the Fe^{3+} species during the polymerization. Acrylonitrile/alkyl methacrylate copolymers doped with ferric chloride showed improved thermal stability at higher temperatures despite of the early weight loss. TGA also showed a multistep degradation in doped copolymers. Heated copolymers did not show the formation of a species other than Fe^{3+}. IR and Mössbauer studies of the samples heated at 500°C showed the formation of α-Fe_2O_3.

The purpose of the work described in chapter V, is to prepare vinyl acetate/methyl methacrylate (V/M), vinyl acetate/ethyl methacrylate (V/E), and vinyl acetate/nbutyl methacrylate (V/B) copolymers by free radical initiated emulsion copolymerization using a semicontinuous batch process. Copolymer composition determined from ^{1}H-NMR spectroscopy was found to be in good agreement with those expected theoretically. The different resonances in ^{13}C-NMR spectra like carbonyl and quaternary carbon have been assigned to comonomer triad sequences with the help of variable composition NMR and were used for calculating alkyl methacrylate centered triad fractions. The methylene carbon resonance of vinyl acetate unit gave information about V centered triad distribution in V/M copolymers, whereas in other copolymers, the resonances giving information regarding the V-centered triads were not properly resolved.

As a different procedure was adopted for the preparation of above samples, they could not be doped with ferric chloride.

C O N T E N T S