NMR STUDIES OF VINYL ACETATE COPOLYMERS

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Dedicated
to my
Brother & Sister-in-law

CERTIFICATE

This is to certify that the thesis entitled,"NMR STUDIES OF VINYL ACETATE COPOLYMERS", being submitted by **Mr Shiv Charan** to the 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. Mr Shiv Charan 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 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 the synthetic vinyl copolymers is of both fundamental and practical importance. The knowledge of copolymer composition and sequence distribution is an important step in the evaluation of their utility. Keeping in view the significance of polymer microstructure, a work was under taken with a purpose to develop the theoretical and experimental basis for characterizing the structure of polymer chains at molecular level.

The thesis consists of six chapters. The first chapter describes the literature survey and briefly summarizes some aspects of the polymer microstructure.

The second chapter describes the experimental procedures for the preparation of homopolymers, copolymers and tercopolymer.The molecular weights of the copolymers and tercopolymer were determined using viscometric technique. The composition of prepared polymer samples were estimated from ^{1}H-NMR spectra of the copolymer/tercopolymers. The composition data was used for the calculation of comonomer reactivity ratios by the methods of Kelen-Tudos(KT)and Error in Variables(EVM) using RREVM computer program.

The third chapter deals with the reactivity ratios and microstructure of (vinyl acetate)/(methyl methacrylate)(V/M), (vinyl acetate)/(ethyl methacrylate)(V/E) and (vinyl actetate)/(butyl methacrylate)(V/B).The copolymer composition was determined by ^{1}H-NMR spectroscopy. The reactivity ratios of these copolymers were calculated by KT method and RREVM program. The reactivity ratios for V/M copolymres are $r_V=0.036\pm0.02$:$r_M=25.6\pm15.21$(KT method) and $r_V=0.045\pm0.017$:$r_M=31.3\pm5.06$(RREVM

computer program). The microstructure of (vinyl acetate)/(methyl methacrylate) (V/M) copolymers was determined by $^{13}C\{^1H\}$-NMR spectroscopy. The resonance signals of carbonyl carbons of V and M units apearing in the regions δ169.8-170.4 ppm and δ175.5-178.2 ppm respectively and the resonance signals of the quaternary carbon of M unit appearing in the region δ43.2-45.2 ppm were used for the determination of the microstructure of V/M copolymers. The Microstructure was obtained in terms of the distribution of V- and M-centered triads. The relative fractions of V- and M-centered triads were found to be in good agreement with those calculated theoretically using the reactivity ratios $r_V=0.036\pm0.022$; $r_M=25.6\pm15.2$ in Harwood's terminal model program and in the Monte-Carlo Simulations. Similarly microstructure was determined for V/E and V/B copolymers. Triad sequence distribution was used to calculate conditional probabilities and number average sequnce lengths. Homonuclear ^1H COSY and NOESY 2D-NMR techniques were used to determine the couplings between different protons in the copolymers. The connectivites between different protons in the V/M copolymer suggest that gauche(+) conformer is more probable. Coploymerization behaviour was investigated by studying triad concentration as a function of conversion as well as by plotting mol percent conversion as a function of copolymer composition for different feeds. It is found that for all these copolymers the copolymerization tends towards a heterogeneous nature at higher conversions with increasing vinyl acetate content in the feed.

In the fourth chapter the reactivity ratios and microstructure of (vinyl acetate)/(methyl acrylate)(V/M), (vinyl acetate)/(ethyl acrylate)(V/E) and (vinyl acetate)/(butyl acrylate)(V/B) has been investigated. ^1H-NMR spectra of copolymers were used to find the copolymer composition. The reactivity ratios of V/M copolymers calculated by KT method and RREVM program are

$r_V=0.04\pm0.03$;$r_M=7.28\pm2.88$ and $r_v=0.04\pm0.01$; $r_M=7.28\pm0.37$. $^{13}C\{^1H\}$-NMR spectra of the copolymers were used to study the microstructure. The methine carbon resonance signals of V and M units appearing respectively in the regions δ66.0-69.7 ppm and δ 37.0-41.3 ppm provided information about the microstructure.The resonance signals of the methine carbons of M unit were differentiated from those of methylene carbons of V unit using C-13 DEPT NMR technique. The V- and M- centered triads were assigned by observing compositional variation in the intensity of resonance signals as well as comparision of the $^{13}C\{^1H\}$-NMR spectrum of the copolymer with those of the homopolymers. Experimental triad distribution in terms of V- and M- centered triads was found to be in good agreement with the theoretical distributions calculated using $r_V=0.04$ and $r_M=7.28$ in Harwood's statistical model and Monte Carlo simulations. Conditional probabilities and number average sequence lengths were also calculated from triad sequence distribution. Connectivities between different protons observed in homonuclear ^1H COSY and NOESY NMR of V/M copolymer suggest the gauche(+) conformer to be more probable in V/M copolymer. Copolymerization behaviour for thses copolymers was also investigated and found to be tending towards heterogeneity at higher copolymer conversions for feeds rich in vinyl acetate.

Copolymers of glycidyl methacrylate are increasing in importance due to their application as speciality copolymers for binding enzymes and microelectronics etc. The fifth chapter is devoted to the determination of reactivity ratios and microstructure of (vinyl acetate)/(glycidyl methacrylate)(V/G). The copolymer composition was calculated from ^1H-NMR spectra of the copolymers. The reactivity ratios for V/G copolymers calculated by KT and RREVM methods are $r_V=0.03\pm0.01$; $r_G=38.9\pm6.20$ and $r_V=0.03\pm0.002$; $r_G=39.5\pm1.97$

respectively. The microstructure of V/G coploymers was determined in terms of V and G centered triads using $^{13}C\{^1H\}$-NMR spectroscopy. The microstructure was obtained from the resonance signals of carbonyl carbons of V and G units appearing as multiplets in the regions δ169.70-170.40 ppm and δ176.6-178.0 ppm respectively. The triad sequence distribution obtained from $^{13}C\{^1H\}$-NMR spectroscopy was found to be in good agreement with the theoretical distributions calculated from Harwood's terminal model program and Monte Carlo Simulations using the reactivity ratios r_V=0.04 and r_G=33.0. The triad sequence distribution was used to obtain conditional probabilities and number average sequence lengths. Connectivities between different protons from homonuclear ^1H 2D COSY suggest that the gauche conformer may be present in the V/G copolymer.

Multicomponent polymerization is increasing in importance because it offers chemical, physical and mechanical properties that differs from copolymers. The sixth chapter investigates into the microstructure of (vinyl acetate)/(methyl methacrylate)/ (acrylonitrile) (V/M/A) tercopolymers. The compostion of the tercopolymers were obtained from ^1H-NMR spectroscopy and was found to be in excellent agreement with the theoretical compostion values calculated using Alfrey and Goldfinger's equation. The microstructure was determined using $^{13}C\{^1H\}$-NMR spectroscopy. The resonance signals were assigned by comparing the tercopolymer spectrum with the spectra of the homopolymers. The resonance signals of the carbonyl carbon of M unit and nitrile carbon of A unit appearing respectively in the regions δ174.5 -180.2 ppm and δ119.7-123.0 ppm were used to study the tercopolymer microstructure. The experimental microstructure was found to be in good agreement with that calculated theoretically using the reactivity ratios r_{MA}=1.42; r_{AM}=0.21, r_{MV}=25.6; r_{VM}=0.04, r_{AV}=4.05; r_{VA}=0.06 in statistical model.

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