SYNTHESIS AND SEQUENCE DETERMINATION OF TRANS-4- ACRYLOYLOXYAZOBENZENE AND TRANS-4-METHACRYLOYLOXYAZOBENZENE BASED COPOLYMERS BY ONE AND TWO DIMENSIONAL NMR SPECTROSCOPY

by
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DOCTOR OF PHILOSOPHY

to the

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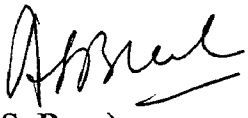
Dedicated
to my
Parents & Wife

CERTIFICATE

This is to certify that the thesis entitled, **"SYNTHESIS AND SEQUENCE DETERMINATION OF TRANS-4-ACRYLOYLOXYAZOBENZENE AND TRANS-4-METHACRYLOYLOXYAZOBENZENE BASED COPOLYMERS BY ONE AND TWO DIMENSIONAL NMR SPECTROSCOPY"**, being submitted by **Mr. M. Thiyagarajan** 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 him. Mr. Thiyagarajan 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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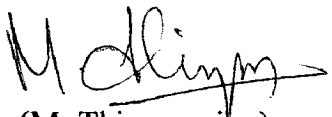
Care has been taken to give proper credit for work of other authors in the literature. I regret my omissions which might have occurred by oversight.



(M. Thiyagarajan)

ABSTRACT

Photoresponsive polymers are used in constructing photoactive devices in several fields such as printing, photolithography and photosensors. A photoresponsive polymer is a speciality polymer having photoreceptor chromophores, which transfer light energy into a change in the conformation of the polymer. The basic idea for controlling the properties of polymers by photoirradiation is to use photoresponsive trigger molecules. Blair et al. described photoresponsive effects in photochromic polyamides in which every monomer unit contains an azo group. However, it is well known that the polymer conformational properties definitely depend on the main chain tacticity. Therefore, in order to get a better insight into the polymer photochromism, Doddrell et al. carried out a systematic investigation of photochromic polymer stereochemistry by $^{13}C\{^{1}H\}$-NMR. This technique is able to provide macromolecular dynamics and the main chain tacticity. Solaro et al. have reported the microstructure of poly(trans-4-methacryloyloxy-azobenzene) using $^{13}C\{^{1}H\}$-NMR spectroscopy. The chiroptical properties and photochromic behavior of the copolymers were reported by Altomare et al.

Keeping in view of the significance of the polymer microstructure, work was undertaken with a purpose to develop the theoretical and experimental basis for characterizing the structure of photochromic copolymer chains at the molecular level. The stereochemical and compositional structure of homopolymers and copolymers were investigated by means of a combination of one and two-dimensional NMR spectroscopy. Traditional techniques (1D experiments) were not always suitable for unequivocal signal assignments. This necessitates the use of two-dimensional NMR techniques especially Homonuclear Double Quantum Filtered Correlation (DQF-COSY) and Heteronuclear Single Quantum Correlation (HSQC) spectroscopy in determining the stereochemical and compositional sequences.

In our present work the microstructure of homopolymer of trans-4-acryloyloxyazobenzene (AB) and trans-4-methacryloyloxyazobenzene (MAB) and various copolymers of these two monomers with methyl methacrylate, vinylidene chloride, styrene and acrylonitrile have been determined by one-dimensional (^1H, $^{13}C\{^1H\}$, and ^{13}C-DEPT NMR) and two-dimensional NMR (Heteronuclear Single Quantum Correlation, Double Quantum Filtered Correlation, Total Correlation Spectroscopy and Nuclear Overhauser Effect Spectroscopy) experiments.

The thesis consists of seven chapters. The first chapter describes the general introduction about the microstructure of the polymers and the review of the literature. It also describes the use of one and two-dimensional NMR spectroscopy for microstructure determination of polymers.

The second chapter describes the experimental procedures for the preparation of monomers, homopolymers and copolymers by solution polymerization using benzoyl peroxide or AIBN as an initiator. The experimental details for the determination of molecular weight by GPC are given. The composition of the trans-4-acryloyloxyazobenzene copolymers and trans-4-methacryloyloxyazobenzene copolymers was determined from ^1H NMR, quantitative $^{13}C\{^1H\}$-NMR spectra and C, H, N elemental analysis. This chapter also gives the detailed description of the one and two-dimensional NMR experiments carried out throughout this research work.

The third chapter deals with the sequence determination of poly (trans-4-acryloyloxyazobenzene) and poly (trans-4-methacryloyloxyazobenzene) prepared by solution polymerization. The microstructure of homopolymers were analysed by one and two-dimensional NMR spectroscopy. Sequence distribution was calculated from $^{13}C\{^1H\}$-NMR spectrum of the homopolymer. ^{13}C DEPT-135 spectrum was used to differentiate the resonance signals of methine and methylene carbon units in the homopolymer. The

triad sequence distribution of homopolymer determined from carbonyl carbon resonance is in good agreement with the triad concentration calculated from the Bernoullian statistical model. 2D Heteronuclear Single Quantum Correlation (HSQC) was used to analyse the complex ^{1}H NMR spectrum. 2D TOCSY, NOESY and DQF-COSY NMR spectrum was used to ascertain the various configurational sequences of the homopolymer.

Chapter four describes the stereochemical and compositional assignments of trans-4-acryloyloxyazobenzene and trans-4-methacryloyloxyazobenzene with methyl methacrylate copolymers. The copolymer compositions were obtained from ^{1}H-NMR spectra. The reactivity ratios of copolymer were calculated using Kelen-Tudos (KT) and non-linear error in variable model (EVM) methods. The reactivity ratios obtained from the KT and EVM methods for trans-4-acryloyloxyazobenzene/ methyl methacrylate (A/M) copolymer are $r_A = 0.6 \pm 0.1$; $r_M = 1.2 \pm 0.1$ and $r_A = 0.6 \pm 0.1$; $r_M = 1.2 \pm 0.1$, respectively. The A- and M- centered triad concentrations were calculated from $^{13}C\{^{1}H\}$- NMR spectra of copolymers and gave good agreement with those calculated from theoretical models and MC simulations. A ^{13}C DEPT-135 spectrum was used to differentiate the resonance signals for methine and methylene carbons in the copolymer. The compositional and configurational sequence assignments were done by 2D HSQC, DQF-COSY and TOCSY experiments. Similar studies were done for trans-4-methacryloyloxyazobenzene / methyl methacrylate copolymers.

Chapter five is devoted to the copolymers of trans-4-acryloyloxyazobenzene and trans-4-methacryloyloxyazobenzene with vinylidene chloride. The trans-4-methacryloyloxyazobenzene / vinylidene chloride (M/V) copolymers of different monomer concentrations were prepared by solution polymerization. The copolymer composition was determined from the $^{13}C\{^{1}H\}$-NMR spectrum. The quaternary carbon of M- and V- centered resonances were used for determining the sequences in terms of the

distribution of M- and V- centered triads. The sequence distribution of M- and V- centered triads determined from quantitative $^{13}C\{^1H\}$-NMR spectra of the copolymer was in good agreement with the triad concentration calculated using first order Markov terminal model, using Harwood's program. The comonomer reactivity ratios determined by both the Kelen-Tudos (KT) and the non-linear error in variable model (EVM) methods are $r_M = 3.59 \pm 0.19$; $r_V = 0.89 \pm 0.07$ and $r_M = 3.76$; $r_V = 0.93$, respectively. The methylene carbon resonance signals have been assigned up to the tetrad levels using 2D HSQC experiments. The inequivalent methylene protons shown in 2D HSQC experiments were confirmed by the geminal couplings of methylene proton observed in the 2D DQF-COSY NMR spectrum. Monte Carlo simulation were also used for determining the triad fractions and for studying the variation of M- and V- centered triads as a function of fractional conversion. Similar investigations were carried out for trans-4-acryloyloxyazobenzene / vinylidene chloride (A/V) copolymers.

The sixth chapter deals with the microstructure determination of trans-4-acryloyloxyazobenzene and trans-4-methacryloyloxyazobenzene with styrene copolymers. The copolymer compositions of trans-4-methacryloyloxyazobenzene / styrene (M/S) copolymers of different monomer concentrations were determined from the percent nitrogen content in the copolymers. The methyl carbons of M- and quaternary carbon of S-centered resonances were used for determining the sequence in terms of the distribution of M- and S- centered triads. The sequence distribution of M- and S- centered triads determined from $^{13}C\{^1H\}$-NMR spectra of the copolymer is in good agreement with triad concentration calculated from statistical model and MC simulations. The comonomer reactivity ratios, determined by KT and EVM method are $r_M = 1.02 \pm 0.12$; $r_S = 0.55 \pm 0.07$ and $r_M = 1.02$; $r_S = 0.54$, respectively. The triad concentrations obtained using the methyl carbon resonance of M- and quaternary carbon resonance of S- monomeric units

were found to follow first order Markov model. The complex ^1H NMR spectrum of M/S copolymers were assigned completely to various compositional and configurational sequences with the help of 2D HSQC and TOCSY experiments. 2D HSQC spectrum shows the presence of inequivalent protons and this was confirmed by the 2D TOCSY spectrum. Similar experiments were carried out for trans-4-acryloyloxyazobenzene / styrene (A/S) copolymer. The comonomer reactivity ratios determined by KT and EVM method are $r_A = 0.27 \pm 0.07$; $r_S = 0.54 \pm 0.09$ and $r_A = 0.26$; $r_S = 0.53$, respectively.

The configurational and compositional sequence of the trans-4-acryloyloxyazobenzene and trans-4-methacryloyloxyazobenzene with acrylonitrile copolymer was given in chapter 7. The copolymer composition was determined for trans-4-acryloyloxyazobenzene / acrylonitrile (A/N) copolymer from the quantitative $^{13}C\{^1H\}$-NMR spectrum. The carbonyl carbon of A- and methine carbon of N- centered resonances was used for determining the sequences in terms of the distribution of A- and N- centered triads. The comonomer reactivity ratios determined by both KT and EVM method are $r_A = 0.39 \pm 0.06$, $r_N = 0.91 \pm 0.11$ and $r_A = 0.41$; $r_N = 0.93$, respectively. ^{13}C-DEPT-135 spectrum was used to differentiate the methine and methylene carbon resonance signals of A- and N- units. The methine and methylene resonance signals have been assigned up to tetrad levels using 2D HSQC experiments. The geminal couplings in the methylene and methine proton region are shown in 2D TOCSY spectrum. Monte Carlo simulation were also used for determining the triad fractions and for studying the variation of A- and N-centered triads as a function of fractional conversion. Similar studies have been carried out for trans-4-methacryloyloxazobenzene / acrylonitrile (M/N) copolymer. ^{13}C-DEPT-135 spectrum was used to differentiate the resonance signals of methine and methylene carbon signals of M- and N- units. The compositional sequences of this copolymer were assigned by 2D HSQC and TOCSY experiments.

CONTENTS

CHAPTER VII TRANS-4- ACRYLOYLOXYAZOBENZENE /ACRYLONITRILE COPOLYMERS TRANS -4- METHACRYLOYL OXYAZOBENZENE / ACRYLONITRILE COPOLYMERS