NMR STUDIES OF STYRENE COPOLYMERS PREPARED BY ATOM TRANSFER RADICAL POLYMERIZATION

by

PUNEETA

DEPARTMENT OF CHEMISTRY

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1. Styrene Copolymers
2. Polymers chemistry

Dedicated

to

My Family

CERTIFICATE

This is to certify that the thesis entitled, **"NMR STUDIES OF STYRENE COPOLYMERS PREPARED BY ATOM TRANSFER RADICAL POLYMERIZATION"**, being submitted by Ms. Puneeta 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. Puneeta 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.

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

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(Puneeta)

ABSTRACT

Polystyrene and its copolymers, due to their high thermal stability, excellent electrical properties and low cost are useful for many commercial applications. Its copolymers with acrylates and methacrylates are of wide interest in many industrial applications especially in paint, adhesives and coatings.

Free radical polymerization is widely used for the synthesis of polymeric materials because of the availability of a wide range of readily polymerizable monomers, mild reaction conditions, and tolerance to impurities. Recent years have witnessed the flourishing of controlled/living radical polymerizations (CRP's). These methods produce 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) has developed into one of the most robust synthetic tool within the spectrum of CRP processes due to its tolerance to a wide range of monomers and solvents of different polarity. 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

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most powerful technique in the determination of microstructure of polymers. Chemical shifts are sensitive to configurational and compositional sequences, thus, different

microstructures can be resolved in the NMR spectrum. Qualitative and quantitative estimation of monomers in copolymers can be done by using various NMR techniques. It is often observed that the macroscopic properties of polymers are critically dependent on the microstructure.

NMR techniques have been extensively used for the microstructure determination of polymers in solutions. These studies are often motivated by a desire to understand structure-property relationships at the molecular level. It is often observed that polymers with similar monomer compositions have different mechanical, thermal, optical or electrical properties as a consequence of differences in microstructure.

One-Dimensional (1D) NMR techniques (^{1}H, ^{13}C{^{1}H}and DEPT NMR) along with Two-Dimensional (2D) NMR has continued to surprise and delight NMR spectroscopists with the range and depth of its problem-solving ability. Owing to the complexity of ^{1}H, ^{13}C{^{1}H} NMR spectra of copolymers, complete assignments are a difficult task. Nevertheless, because of the high information content of fully interpreted spectra it remains an important area to investigate. 1D NMR techniques especially DEPT NMR techniques has been used to distinguish various methyl, methylene and methine signals. Further, 2D NMR methods have been extensively used in the unambiguous assignments of ^{1}H, ^{13}C{^{1}H} NMR spectra of polymers. The 2D NMR techniques like that involves directly attached carbon-proton by Heteronuclear Single Quantum Coherence (HSQC), proton-proton coupling by Total Correlation Spectroscopy (TOCSY) and long range coupling between heteroatoms not attached directly by Heteronuclear Multiple Bond Correlation (HMBC) NMR experiments can help in unambiguous stereochemical and compositional assignments of ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of the polymers.

Monomer sequence distributions have a direct bearing on the chemical and physical properties of copolymers. Keeping in view the importance of polymer microstructure, a work was undertaken with a purpose to understand the experimental basis for characterizing the structure of copolymer chains at the molecular level.

The aim of the thesis is to synthesize styrene copolymers with an intramoleculary heterogeneous chemical composition distribution using ATRP and to determine their microstructure by 1D and 2D NMR techniques.

The thesis consists of five chapters. Chapter I contains the introduction to various types of polymerization, significance of controlled radical polymerization and the importance of ATRP. Literature survey in the field of ATRP has been reviewed. This chapter also describes the general introduction about the microstructure and the review of literature related to NMR of polymers. It describes the use of 2D NMR spectroscopy (especially HSQC, TOCSY and HMBC) for microstructure determination. A general introduction to the polymer microstructure with special emphasis on the sequence distribution is included.

Chapter II includes the experimental details for the preparation of homopolymers and copolymers by ATRP. It also includes experimental details for the preparation of block copolymers. Experimental details of the Molecular weight determination by GPC are given. The composition of the copolymers was determined from ^{1}H NMR. A description for the 1D (^{1}H, $^{13}C\{^{1}H\}$and DEPT NMR), and 2D (HSQC, TOCSY and HMBC) NMR experiments are incorporated.

Chapter III deals with the sequence determination of the styrene/methyl acrylate (S/M), styrene/ethyl acrylate (S/E) and styrene/n-butyl acrylate (S/B) copolymers. All these copolymers were prepared by ATRP. Molecular weights of the copolymers have been determined by Gel Permeation Chromatography (GPC). Percentage conversion was determined gravimetrically. It has been found that molecular weights of the copolymers increase with increase in percentage conversion. As the percentage conversion increases from 9% to 80%, the molecular weight increases from 8000 to 60000 with polydispersity remaining low (1.12-1.25). The composition of copolymers has been determined from ^{1}H NMR. The copolymer composition data has been used to determine the reactivity ratios by Kelen-Tudos (KT) and nonlinear error in variables methods (EVM) methods. The reactivity ratios calculated for S/B copolymers are : $r_s = 0.87 \pm 0.10$, $r_b = 0.25 \pm .01$ and $r_s = 0.87$, $r_{b=}$ 0.25 from KT and RREVM, respectively. The microstructure was obtained in terms of the distribution of S-, B-, E-, and M- centered triad sequences from $^{13}C\{^{1}H\}$ NMR spectra of the copolymers. In the case of S/B copolymers, carbonyl and the quarternary carbon resonances of B and S units respectively, have been used to assign the triad compositional sequences and to determine triad concentration. There is a good agreement between the experimentally (NMR) determined triad fractions and those calculated from theoretical methods. ^{13}C $\{^{1}H\}$ NMR spectra of these copolymers show that the methylene and methine signals of the main chain are compositional sensitive and highly overlapped. Even the Distortionless Enhancement by Polarization Transfer (DEPT) was not able to assign the complex and overlapping signals. Assignments of the various resonance signals were done with the help of

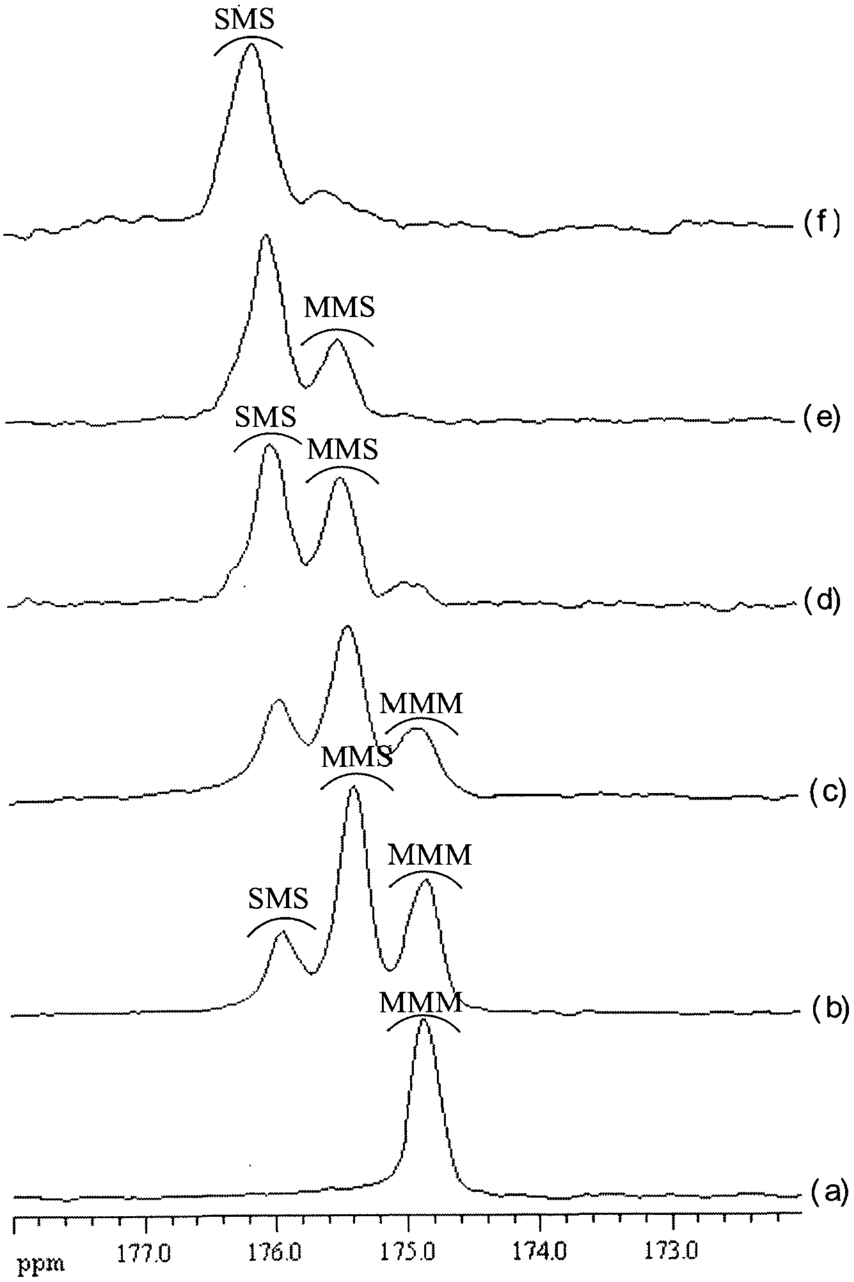

Fig. I Expanded carbonyl carbon of the M unit in the $^{13}C\ \{^{1}H\}$ NMR spectra of the styrene/methyl acrylate copolymers in $CDCl_3$ at 25°C: a) poly(methyl acrylate), b) $F_M = 0.69$, c) $F_M = 0.63$, d) $F_M = 0.50$, e) $F_M = 0.39$, and f) $F_M = 0.26$.

HSQC, TOCSY and HMBC experiments. Heteronuclear 2D HSQC was used to simplify the complex ^{1}H NMR spectra of the copolymers. The methylene carbon resonances of B and S units have been assigned to dyad compositional sequences. The 2D TOCSY experiments were used to make unambiguous assignments from the various coupling between the protons of the copolymers. The vicinal coupling between the methine protons in the B- and S- centered triads with the methylene protons in the BB, BS, and SS dyads have been assigned by TOCSY spectra of the different copolymer composition. Analysis of the two or three bond order proton/carbon coupling was carried out from 2D HMBC experiments. Carbonyl carbon has been assigned upto triad level. This chapter also includes the microstructure determination of poly(n-butylacrylate). Poly(n-butylacrylate) was synthesized by ATRP using CuBr/N,N,N',N',N"-pentamethyldiethylenetriamine as catalyst and Methyl 2-bromopropionate as initiator at 60°C. ^{1}H NMR spectrum of poly(n-butylacrylate) is very complex and overlapping. Methylene groups of the pendant chain overlaps with the main chain methylene group and thus, it is difficult to determine the structure of the polymer. It can only be assigned with the help of 2D NMR techniques, such as, HSQC, TOCSY and HMBC.

The sequence distribution and microstructure of the S/M, S/E and S/B copolymers and poly(n-butyl acrylate) are analyzed by various 1D and 2D NMR techniques. The copolymers with controlled molecular weight and narrow polydispersities are obtained. As the length of pendant group in the copolymers increases, the spectra become more complex. Various compositional and configurational sequences in the copolymers are unambiguously with the help of

HSQC and TOCSY NMR experiments. Further, various long range couplings are assigned with the help of HMBC. The assignments of the carbonyl carbon have been reaffirmed with the help of HMBC spectra.

Chapter IV deals with the NMR studies of the styrene/methyl methacrylate (S/M), styrene/ethyl methacrylate (S/E) and styrene/butyl methacrylate (S/B) copolymers. These copolymers were synthesized by ATRP. Molecular weight distributions were determined by GPC. It was found that the molecular weight increases with increase in conversion. Polydispersity of the copolymers is very low i.e. 1.1-1.3. The composition of the copolymer was determined by the help of ^{1}H NMR. The reactivity ratios calculated for S/M copolymers are: r_s= 0.64± 0.08, r_m= 0.63 ± 0.08 and r_s= 0.66, $r_{m=}$ 0.65 from KT and RREVM, respectively. The α-methyl and carbonyl carbon resonances were found to be compositionally and configurationally sensitive. Methine group of the Styrene unit was assigned up to triad level of compositional sensitivity for carbon resonances. The assignments made in ^{13}C {^{1}H} NMR spectra were further confirmed by 2D HSQC and TOCSY NMR experiments. 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 and configurational 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. The main striking feature of the ^{1}H spectra of the S/M copolymers is the splitting of the methoxy protons due to the various compositional and configurational sequences. The compositional and configurational tacticity in methoxy protons has been assigned unambiguously with the help of HMBC in which, it shows coupling with carbonyl carbon. A complete spectral assignment has been done for S/M, S/E and S/B copolymers with the correlation of 1D (^{1}H, ^{13}C{1H}, DEPT-135) and 2D (HSQC, HMBC) NMR spectroscopy. As the length of pendant chain increases, the reactivity of

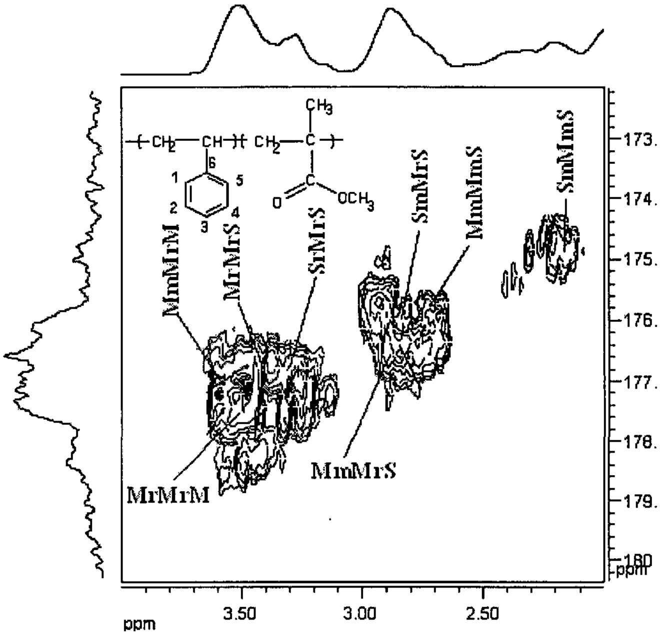

Fig. II Expanded 2D HMBC NMR spectrum of the S/M copolymer (F_M = 0.51), indicating the couplings of the carbonyl carbon with the methoxy region in $CDCl_3$ at 25 °C.

methacrylate increases as compared to styrene, but at the same time spectra becomes more complex. The compositional and configurational tacticity in α-methyl and methoxy protons has been assigned with the help of HMBC in which, it shows coupling with carbonyl carbon.

Chapter V illustrates the synthesis of block copolymers of styrene/methyl acrylate, styrene/ethyl acrylate, styrene/n-butyl acrylate and styrene/methyl methacrylate of different sequence lengths. These block copolymers were synthesized by ATRP using halogen exchange technique and CuBr/N,N,N',N',N"-pentamethyldiethylenetriamine as catalyst. Formation of the block copolymers was confirmed by the GPC traces of the polystyrene segment and block copolymer. The polydispersities of homopolymer and diblock copolymers were both low, $M_w/M_n < 1.3$. Further, ^1H and $^{13}C\{^1H\}$ NMR and HSQC also confirms the formation of block copolymers. Microstructure of the block copolymer was determined with the help of 1D and 2D NMR techniques. ATRP has been used to synthesize intramolecularly heterogenous copolymers of styrene with acrylate and methacrylates. Well-defined blocks with narrow molecular weight distributions have been synthesized. Monomodal nature of the molecular weight distribution curve indicates the existence of block copolymer. The information obtained from NMR has been used to ascertain the formation of block copolymers, to find the relative incorporation of the monomer units in the polymer chain and to determine the tacticity of the polymer blocks. The information from the two dimensional spectra, supported by the one dimensional spectral information, has been used to study the end group linkages.

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