NMR STUDIES OF ACRYLATE AND METHACRYLATE COPOLYMERS

by

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DEPARTMENT OF CHEMISTRY

Submitted
in fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

MARCH, 2007

NMR spectroscopy
Acrylate copolymers
Methacrylate copolymers

Dedicated
To
the Almighty
&
my family

Certificate

This is to certify that the thesis entitled, "NMR STUDIES OF ACRYLATE AND METHACRYLATE COPOLYMERS", being submitted by Ms. Sonia Gandhi to Indian Institute of Technology, Delhi, for the award of the Degree of Doctor of Philosophy, is a record of bonafide research work carried out by her. Ms. Sonia Gandhi has worked under my supervision and guidance and has fulfilled all the requirements for the submission of a Ph.D. thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of the 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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Acknowledgments

Firstly, I would thank "god almighty" for giving me strength, high spirits and showering all his blessings during the entire tenure of my research work.

I express my heartfelt and earnest thanks to my research supervisor, Prof. A. S. Brar who has acted as a major driving force and a source of inspiration at each step of my research work. The accomplishment of this thesis work is the result of his words of wisdom and enlivening guidance. He not only provided me with valuable suggestions and continuous guidance for the completion of my research work and writing of the thesis, but has also given fatherly and friendly guidance at times when I felt discouraged and lost. He is the person whom I would sincerely like to thank and give all my respect.

I wish to thank Prof. Blümich (ITMC, RWTH-Aachen, Germany) for providing me his expert guidance, inspiration and encouraging environment during my stay in Germany. Prof. D. Demco is the one who introduced me to the captivating world of Solid-State NMR. He is the one who guided me and showed me the direction for carrying out research work in Aachen. He helped me in all possible ways to make my life simpler and comfortable and never let me feel nostalgic during my stay. All the appreciable research work that I have done during my stay in Aachen is truly a result of his motivation and hard work.

I thank Prof. U. K. Nadir and Prof B. Jayaram (Head of the Department) for providing facilities and access to the instrumentation lab. I also wish to thank Prof. R. Shankar for encouraging to work harder.

Special thanks to all my teachers from Miranda House, Delhi University who laid the cornerstone and helped in my academic growth.

I wish to thank Mr. Munna Lal and Mr. R. K. Singh, lab technicians in NMR lab for being co-operative. I acknowledge the support given by Mr. Agarwal, Mrs. Shanta, Mr. Sharma, Mr. Gulani and Mr. Kuldip of Instrumentation lab and Mr. Sehgal and Mr. Singh of stores.

The time spent with my labmates-Gurmeet, Meghna, Sukhdeep and Tripta are the most memorable and treasured time during my research. Gurmeet taught us all the aspects of NMR starting from handling the NMR instrument to assigning all the complex spectra. Meghna is the one who has actually been a great support in both academic and personal front. I would sincerely thank her for being there and showing patience to listen to all me problems and showing me the right direction whenever I felt ungratified. Sukhdeep helped me in doing ATRP experiments when I had no clue how to go about it and has always been there for me whenever I looked upon her. Tripta has always tried and pushed me to be self-dependent and the credit for my memorable trip to Aachen goes to her. I thank Jaspreet for being a great pal during the last days of my research and tolerating my temper very courteously. Ashok, the only junior, for maintaining lively and frolic environment in the lab. I wish him all the best things in life. I also wish to thank Pravin and Puneeta for their co-operation and support.

I would like to thank my friends from Aachen- Claudia, Christian, Alina, Adi, Nicol, Ljuba and Maria for being supportive and helping me out with Solid-tate NMR. Thanks to Pooja and Vishal for not letting me feel nostalgic.

I sincerely wish to thank Raj who had always worked hard towards the tterment of my personality and intellectual growth showing me positive ection always and has shown lot of patience towards my temperament encouraging me to believe in myself, enhancing my confidence. Rajeshree, somebody more than a friend and a person who has always showered me with her warmth and affection. Shelly with whom I had a gala time during my hostel days at IIT. Deepshikha, a great friend from school to M.Sc. days has always encouraged me to work harder.

Finally, last but not the least, I thank my parents for their constant support, graceful sacrifices and longanimity. I am fortunate enough to have parents like them, who have been a pillar of strength and have always pampered me with their care and affection fulfilling all my desires. They have stood by me through all thick and thins. Thanks for being there for me.

Sonia Gandhi
(Sonia Gandhi)

Abstract

Carbazole based polymers have attracted much attention due to its potential applications as photorefractive materials. These polymers possess optical properties and good hole transporting ability in light-emitting devices owing to its photoconducting and electro-optical properties, which in turn are essential properties for materials to be photorefractive. Photorefractive properties are possessed by these kinds of copolymers due to photoconductivity combined with non-linear optical activity (NLO). Photorefractivity is enhanced in the copolymers containing ring substituted carbazolyl pendant group due to the generation of charge carriers via intra molecular charge transfer complex. The NLO response makes these copolymers interesting for several applications in the field of optical communication, optical switching and optical signal processing.

Copolymerization with electron acceptor monomers such as methyl acrylate, methacrylonitrile can be used as a tool to improve the physical, chemical and optical properties of these copolymers. Enhancement of non-linear optical response is achieved when these electron acceptor groups are copolymerized wit carbazole containing units.

Structure-property relationship can be established by determining th microstructure, which in turn is essential to study the photo physical properties o the copolymer. High-resolution 1D and 2D NMR have proved to be one of t most informative and revealing techniques for the investigation of polym microstructure.

Various acrylate, methacrylate copolymers can be synthesized via At Transfer Radical Polymerization (ATRP), which is advantageous o

conventional free radical polymerization in terms of control over the molecular weight distribution, the copolymer composition, and the architecture thus making it more potential and industry-friendly. ATRP has also shown to be more versatile with respect to synthesis of novel architectures like block, gradient, graft and star copolymers. Solid-State Spin Diffusion NMR has been used to study the morphology and get the domain sizes of various components present in the diblock coplymers. The interplay between microscopic and mesoscopic properties of diblock copolymer which can be studied by ^{13}C $T_{1\rho}$ measurements in the rotating frame is helpful for a better assessment of the role in the mechanical properties of these systems.

The thesis consists of five chapters. ***Chapter 1*** deals with the literature survey done on the industrial importance of ring substituted carbazole based photoconducting polymers in terms of their photorefractivity. The literature survey shows the need to make these polymers industrially more viable in terms f their processability, charge transport and thin-film making properties by having control over molecular weight, structure etc, which in turn could be achieved by polymerization. The crucial part played by NMR in determining the icrostructure has been highlighted. Also the advantages of ATRP over nventional radical polymerization has been discussed which has been further d to synthesis block copolymers. The approach adopted in this research work ng with its contribution to the field of polymers and NMR has been rporated. Various aspects of solid-state spin diffusion NMR studies have been ussed. Also studies done and advantages of ^{13}C $T_{1\rho}$ measurements in the ing frame to study the morphology of block copolymers have been dealt.

arious assignments in $^{13}C\{^{1}H\}$ NMR were done by determining peak areas using orentzian curve-fitting and then correlating them with peak areas calculated on he basis of Bernoullian statistics. There was good agreement between the two sets f values, suggestive of the assignments being authentic.

The backbone methylene and α-methyl were assigned to dyad and triad configurational sequence, respectively. These assignments were further justified with the help of 2D HSQC and TOCSY experiments. The higher carbon/proton bond order couplings for $-OCH_2$, $-NCH_2$ and aromatic region were studied by HMBC. Explicit assignments of carbon/proton resonances and the analysis of different connectivities were done using 2D NMR spectroscopy thus establishing the microstructure of the homopolymer.

A series of (9-ethyl-carbazol-6-yl)methyl methacrylate (E)/ methyl acrylate (A) copolymers were synthesized by free-radical polymerization. The reactivity ratios for different compositions of E/A copolymers obtained by KT and RREVM methods are $r_E = 1.16 \pm 0.02$, $r_A = 0.69 \pm 0.01$ and $r_E = 1.18$, $r_A = 0.68$, respectively. The microstructure of E/A copolymers was analyzed by 1D (^{1}H, $^{13}C\{^{1}H\}$, DEPT-45, 90, 135) and 2D (HSQC, TOCSY, HMBC) NMR spectroscopy. The complex and overlapped β-methylene and methine region has been resolved by 2D HSQC and 2D TOCSY NMR studies. Complete spectral assignments for carbonyl region have been done by 2D HMBC studies. Tg for different compositions of E/A copolymers has been determined by DSC showing a decrease in Tg with decreasing E content due to increasing flexibility of the polymeric chain.

Chapter 2 contains the description of the various experimental techniq used during the current research work. It describes the details of various st involved in the synthesis of (9-ethyl-carbazol-6-yl)methyl methacrylate and (ethyl-carbazol-6-yl)methyl acrylate monomers. Various experimental details a conditions involved in homo and copolymerization for these monomers have bee reported.

The experimental details for the various 1D (^{1}H, $^{13}C\{^{1}H\}$, DEPT-45, 90 and 135) NMR and 2D (Heteronuclear Single Quantum Correlation (HSQC), Total Correlation Spectroscopy (TOCSY) and Heteronuclear Multiple Bond Correlation (HMBC)) NMR experiments have been incorporated. The details of the reactivity ratio calculations both statistically and experimentally along with the calculations of copolymer compositions from the intensities of signals in ^{1}H NMR spectra have also been reported. Amongst various characterization techniques, Gel Permeation Chromatography (GPC) for the determination of molecular weight and molecular weight distribution and Differential Scanning Calorimetry (DSC) for thermal studies have been used. A brief overlay of the synthesis of Styrene (S)/Methyl methacrylate (MMA) diblock copolymers via Atom Transfer Radical Polymerization (ATRP) have also been reported. The experimental details of Solid-state Spin diffusion NMR and ^{13}C $T_{1\rho}$ measurements have been discussed.

Chapter 3 deals with the investigation to elucidate the complete microstructural features of poly((9-ethyl-carbazol-6-yl) methyl methacrylate) using 1D and 2D NMR techniques and assign methylenes, α-methyl and aromatic region of the homopolymer. Signals assignment to different carbon resonances were done using $^{13}C\{^{1}H\}$ NMR in conjugation with DEPT-135 spectrum. The

Chapter 4 discusses in details the microstructure of poly((9-ethyl-carbazol-6-yl)methyl acrylate) synthesized by free-radical polymerization. 1D (^{1}H, ^{13}C{^{1}H} and DEPT) and 2D (HSQC and TOCSY) NMR techniques were used to resolve the overlapping proton and carbon spectra of poly((9-ethyl-carbazol-6-yl)methyl acrylate). The backbone methylene carbon resonances were assigned to dyad configurational sequences with the help of HSQC and TOCSY NMR spectra and thus microstructure of the polymer was established.

A series of ((9-ethyl-carbazol-6-yl)methyl acrylate) (C)/ Methacrylonitrile (N) copolymers were synthesized using free-radical polymerization. The reactivity ratios obtained by KT and RREVM methods for different compositions of C/N copolymers were found to be r_C= 0.31±0.03, r_N=0.80±0.02 and r_C= 0.35, r_N= 0.83 respectively. 1D (^{1}H, ^{13}C{^{1}H}, DEPT- 45, 90, 135) and 2D (HSQC, TOCSY HMBC) NMR spectroscopy were used to analyze the microstructure of C/N copolymers. The overlapped β-methylene, methine and α-methyl regions we assigned to dyad and triad configurational and compositional sequenc respectively which were further strengthened by 2D HSQC and TOCS experiments. The higher carbon/proton bond order couplings between nit carbon and α-methyl protons were studied by 2D HMBC NMR experiments.

Tg for different compositions of C/N copolymers has been determine DSC showing a decrease in Tg with decreasing C content due to increa flexibility of the polymeric chain. Thus, introduction of monomer N re flexibility and prevents tight packing between the polymeric chains resulting increase of free volume in the chains thereby lowering the Tg.

Chapter 5 deals with the characterization of the morphology and domain sizes of PS-*b*-PMMA block copolymers using Solid-State spin-diffusion NMR. A detailed picture of the morphology of PS-*b*-PMMA was obtained by the spin-diffusion experiments using double-quantum dipolar filters. This type of filter is advantageous as it selects the magnetization from rigid domain of the block copolymer. The sizes of rigid, interface and mobile components were estimated based on general analytical solution of the spin-diffusion in a lamellar morphology composed of three domains. Domain size dependency on molecular weight was established and the studies on interface of PS-*b*-PMMA were carried out for the first time. The correlation of the long period on the block copolymer indicates a good agreement with the theoretical predictions $d_{\mathrm{long}} \propto Mn^{2/3}$.

The molecular motions for ^{13}C in PS-*b*-PMMA have been measured using
C CP/MAS NMR technique. ^{13}C $T_{1\rho}$ spin-lattice relaxation times in the rotating
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ntribution from both rigid and mobile component. Hence ^{13}C NMR has
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