CARBAZOLE- BASED POLYMERS: SYNTHESIS, STEREOREGULARITY CONTROL AND NMR STUDIES

by

MEGHNA MARKANDAY

DEPARTMENT OF CHEMISTRY

Submitted
in fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

MAY, 2006

Aromatic compounds - Carbazolyl group - NMR studies
Copolymers - Carbazolyl ethyl acrylate - Methyl acrylate

TH

678.764.43:543.42
MAR-C

Dedicated

To

The Almighty

Certificate

This is to certify that the thesis entitled, "CARBAZOLE- BASED POLYMERS: SYNTHESIS, STEREOREGULARITY CONTROL AND NMR STUDIES", being submitted by Ms. Meghna Markanday 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. Meghna Markanday 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.

15/6/06

(A. S. Brar)
Thesis Supervisor
Professor
Department of Chemistry
Indian Institute of Technology,
Delhi
Hauz Khas
New Delhi – 110016
INDIA

Acknowledgements

The very thought of the driving force behind my being – God Almighty-fills me with profound gratitude. No words are enough to express the love and kindness He has showered on me in the form of His blessings. In times of doldrums, when I felt absolutely alone, He stepped in silently and anchored me on to safe shores. Without His blessings I could not have accomplished even a bit.

The constant support and inspiration provided by my Supervisor, Prof. A. S. Brar, was invaluable in seeing me through my research work. He always stood as a guiding light showing me the path when I felt completely lost. He not only discussed my research problems but also extended a warm fatherly support in rough times. The discussions I had with him and especially his words," Shubh karm kar aur kabhi na dar" shall always stay with me as lessons for life.

I wish to thank Prof. H.M. Chawla and Prof. U.K. Nadir (Head of the Department) for providing all the facilities and access to the instrumentation. I wish to extend my special thanks to Prof. R.C. Anand and his Research Associate Dr. Archana, who during the initial stages of my research helped me with organic synthesis.

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

I thank my seniors Dr. Pradhan, Dr. Anil and Dr. Manpreet for sharing their knowledge and experiences in research work and NMR. I wish to extend a special thanks to Dr. Manpreet, who is a warm person and made me feel quite

comfortable in the lab during the early days of my Ph.D. The four people without whom the period of my research work would have been dull and gloomy are Gurmeet, Sukhdeep, Tripta and Sonia. They are the ones who added all the sparkle to my research scholar days. We have shared a great chemistry and the times spent with them will always come back to me as the "golden days" of my life.

Gurmeet, a senior in lab and a great friend, is a person on whom one can always bank upon. His sensibility, thoughtfulness and approach towards handling problems are unparalleled. His fruitful insights always came useful. I can never forget the times when I rushed to him without a second thought for any technical assistance.

Sukhdeep holds a very unique place in my life. The special bond of friendship we shared is very precious to me. She is a person one meets once in a lifetime. The ways in which she has touched my life are countless. Whenever I lost faith, she imbibed me with all the optimism and confidence. I thank God for blessing me with a friend like her.

Tripta and I clicked well the very first time we met. She is a person I could identify with in so many aspects. Being caring and thoughtful comes naturally to her. We have sailed through many stages of research work together. I shall always cherish the times spent with her and especially the coffee-breaks, without which it was impossible to feel rejuvenated.

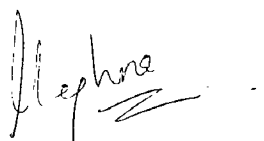
Sonia though is my junior but we never felt any kind of senior-junior divide. She has been a great pal. I cannot think of the last stages of my research work without her company. It was always great fun to tease and bully her!

I thank Jaspreet, Mr. Vivekanand, Ashok, Pravin and Punita, my labmates, for being always quite supportive.

Vijayata, Sanghamitra and Deepti are amongst the three of my best friends since college days. They have rightly proved the saying, "good friends are like stars, you do not always see them, but you know they are there always!"

My grandparents have been a constant source of inspiration and have showered their blessings on me always. They have experienced all my anxieties, thrills and success as their very own. I always found them by my side to laugh and cry. Their enormous moral support sailed me through the roughest times in life. I also wish to extend my immense gratitude to my aunt who has always motivated me in her own ways.

Finally, last but not the least; I thank my parents for being an anchor in my life. Without the constant support of my parents it would not have been possible to accomplish any goal. My father has always stayed as a protective figure still treating me like his little girl. My mother has stood behind me through all thick and thins. Her unnerved confidence in me always kept me in high spirits. She has always been a pillar of strength to me. My younger sis Manvi has been a combination of a little angel and mischievous Satan in my life. Her bubbly nature and childlike innocence clubbed with all the meaningful gestures are overwhelming.



(Meghna Markanday)

Abstract

Carbazole-based materials have attracted much attention, in last decade, as molecular electronic materials and find widespread application as photoconductors, field effect transistors, organic photorefractive materials and components of electroluminescent devices. These materials also exhibit high thermal, chemical, environmental and morphological stability. The factors making these carbazole-based materials as very attractive for industry can be investigated by considering the two basic properties of fully aromatic carbazolyl group viz. easy oxidizability of N atom and its ability to transport positive charge centers via the radical cation species.

It is a well established fact that the polymer properties are determined by molecular properties like molecular weight, molecular weight distribution, chemical composition, stereochemical sequence of copolymer chains, degree of cross-linking etc. Thus, in order to harness their potential to the fullest a control on structure becomes a fundamental requirement.

Conventional free-radical polymerization of acrylates and methacrylate polymers does not allow any precise control over molecular properties and structure. Hence, there arises a need of a different polymerization technique. Living anionic polymerization has offered opportunities to tailor-make model macromolecules with well-defined structures of technical interest. After much speculation classical anionic initiators were picked to synthesize homo- and co-polymers of 2-N-carbazolylethyl(meth)acrylate.

NMR spectroscopy has emerged as a powerful tool for determining the polymer structure at the micro level. Various one (^{1}H, $^{13}C\{^{1}H\}$, DEPT-135, 90,

45) and two dimensional (HSQC, TOCSY, HMBC) NMR techniques were utilized for a comprehensive analysis of microstructure.

The thesis consists of five chapters. A brief Introduction about the current research work and the literature reported in this area has been given in ***Chapter 1***. The chapter reveals the industrial importance of carbazole-based photoconductors along with the current scenario of research on various organic photoconductors. Literature survey done reflects the need of a control on various properties of these polymers like structure, molecular weight, glass transition temperature etc. in order to make them industrially more viable in terms of their processability, charge transport and thin-film making properties. Anionic polymerization has played an eminent role in achieving control on tacticity. Various aspects of anionic polymerization have been reviewed. The crucial part played by NMR in determining the microstructure has been highlighted. Also, the approach adopted in this research work along with its contribution to the field of polymers and NMR has been incorporated.

Chapter 2 contains the experimental details of the research work done. This chapter gives a brief overlay of the various experimental techniques and methods used during the entire course of current research work. The detailed synthesis of the monomers 2-N-carbazolylethyl acrylate and 2-N-carbazolylethyl methacrylate has been reported. The experimental details about the optimization of reaction conditions for homopolymerization and copolymerization both via free-radical and anionic polymerization has been given.

Amongst various characterization techniques, Gel Permeation Chromatography (GPC) for determination of molecular weight and molecular

weight distribution and Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) for thermal studies have been used. The experimental details for the various 1D (^1H, $^{13}C\{^1H\}$, 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 along with the calculations of copolymer compositions from intensities of signals in ^1H NMR spectra have also been reported.

Chapter 3 investigates for the first time the effectiveness of t-C_4H_9MgBr as an initiator for the synthesis of a stereoregular polymer containing bulky pendant moiety viz. poly(2-N-carbazolylethyl methacrylate) via anionic polymerization. Analytical evaluation of stereoregularity in this homopolymer along with end-group analysis has been done using 2D NMR spectroscopy. Poly(2-N-carbazolylethyl methacrylate) with varying degree of tacticities was synthesized by anionic and free radical polymerization. 2,2' azobisisobutyronitrile (AIBN) and t-C_4H_9MgBr were used as initiators for free-radical and anionic polymerizations, respectively. Molecular weight distribution was determined by Gel Permeation Chromatography (GPC). However, any attempts towards preparing homopolymer of the corresponding acrylate viz. poly(2-N-carbazolyethyl acrylate) using t-BuMgBr failed completely.

The mechanism involved in the anionic polymerization of 2-N-carbazolylethyl methacrylate by the initiator t-C_4H_9MgBr was also investigated with the help of various NMR techniques. An exhaustive analysis of the microstructure with unambiguous assignments has been reported along with a

comparison with poly(2-N-carbazolylethyl methacrylate) synthesized by free radical polymerization. The validity of these assignments has been tested and confirmed by calculations using statistical relationships.

Signal assignments to different carbon resonances were done using $^{13}C\{^{1}H\}$ NMR in conjunction with DEPT-135 spectrum. The various assignments in $^{13}C\{^{1}H\}$ NMR spectrum were done by determining peak areas using Lorentzian curve-fitting and then correlating them with peak areas calculated on the basis of Bernoullian statistics. There was a good agreement between the two set of values, suggestive of the assignments being authentic. The peak splittings for α-methyl carbon resonances were used to achieve tacticity assignments up to the pentad level. It was seen that the chemical shift value of mr triad of sample (a) was not coincident with that of sample (b). This reflects that the ^{13}C NMR chemical shifts of vinyl polymers are stereosequence dependent as the local conformation in the vicinity of each resonating ^{13}C nucleus is sensitive to stereoregularity.

The β-methylene carbon of the main-chain showed configurational sensitivity up to the tetrad level. 2D Heteronuclear Single Quantum Coherence (HSQC) spectrum along with Total Correlation Spectroscopy (TOCSY) further, helped in making complete spectral assignments and strengthening them. The 2D Heteronuclear Multiple Bond Coherence (HMBC) studies proved highly beneficial in resolving the configurational sensitivity of the non-protonated carbons viz. the quaternary and carbonyl carbon up to pentad level.

The propagation was very slow as compared to the initiation reaction, and the rate of the polymerization fitted first-order plots indicating the living character of polymerization. Fast initiation and slow propagation along with the living

character are responsible for a low PDI. High degree of isotacticity (P_m = 0.8) was achieved which was comparable to that achieved in PMMA. The glass transition temperature (T_g) was found to be lower than the traditional photoconductive polymers which meant an easier processing.

Chapter 4 deals with the evaluation of efficacy of the classical initiator, t-C_4H_9MgBr, in the anionic copolymerization of a bulky monomer viz. 2-N-carbazolylethyl methacrylate with methyl acrylate and methyl methacrylate for the first time. Various experimental parameters involved were optimized to achieve an enhanced control on the stereoregularity of the resulting polymers. Isotactic random and block copolymers were prepared.

A series of 2-N-carbazolylethyl methacrylate and methyl acrylate copolymers with varying compositions and tacticity were synthesized via anionic polymerization with t-C_4H_9MgBr and free radical polymerization using α, α'-azobisisobutyronitrile as an initiator. Copolymers resulting from free-radical polymerization were predominantly syndiotactic (rr > 90%). While, anionic polymerization with t-BuMgBr led to isotactic stereoregulation of these copolymers. Isotactic random and block copolymers were prepared. The copolymer compositions containing higher proportions of methyl acrylate in poly(2-N-carbazolylethyl methacrylate-co-methyl acrylate) were also obtained in low yields. The polymerization of methyl methacrylate with the living anion of isotactic poly(2-N-carbazolylethyl methacrylate) formed with t-C_4H_9MgBr gave an isotactic block copolymer with unimodal MWD and proved the livingness of the system. Highly encouraging results were obtained when 2-N-carbazolylethyl methacrylate was copolymerized with MMA. Almost 100% isotacticity was

achieved. The 0.5 / 0.5 composition was analyzed in depth. The various experimental parameters like, solvent used for polymerization and temperature were optimized. It was found that ideally higher conversion is achieved at very low temperatures (-60°C). The solvent for polymerization was also varied and it was found that almost similar degree of tacticity was achieved in DCM and toluene, but yields go down in case of THF. Thermal behavior of these copolymers was analyzed. The glass transition temperature was found to vary with change in tacticity as well as composition.

Chapter 5 discusses in detail the sequence determination and stereoregularity in 2-N-carbazolylethyl acrylate / methyl methacrylate copolymers using 2D NMR spectroscopy. A control on glass transition temperatures of these random copolymers was achieved by varying their compositions. A series of 2-N-carbazolylethyl acrylate (C) and methyl methacrylate (M) copolymers with varying compositions were prepared in toluene at 60°C using AIBN as an initiator. The molar outfeed ratio (F_C) for various compositions was determined from ^{1}H NMR spectra. Reactivity ratios calculated using Kelen-Tudos (KT) and non-linear error in variable (RREVM) methods were found to be r_C = 0.43±0.8 and r_M=2.78±0.52. Molecular weight distribution was determined by Gel Permeation Chromatography (GPC). The α-methyl carbon of M unit showed splitting up to the pentad level in $^{13}C\{^1H\}$ NMR spectra and was found to be sensitive to the variation in C/M copolymer compositions.

The backbone methylene and carbonyl carbons of both M and C unit along with α-methyl carbon of the M unit showed both compositional and configurational sensitivity. Distortionless Enhancement by Polarization Transfer

(DEPT) helped in differentiating the methylene carbon signals from the methine and methyl carbon resonances. 2D Heteronuclear Single Quantum Coherence (HSQC) and 2D Total Correlation Spectroscopy (TOCSY) were used in tandem to deduce all spectral assignments. 2D Heteronuclear Multiple Bond Coherence (HMBC) played an important role in studying the stereoregularity of the carbonyl carbon which was found to be sensitive up to the pentad level.

The glass transition temperature (Tg) of various C/Mcopolymer compositions were found to vary with change in composition as seen in Figure 8. It was observed that the T_g of various compositions of these copolymers varied between the T_g of the respective homopolymers viz.poly(2-N-carbazolylethyl acrylate) and poly(methyl methacrylate).

Comparing the Tg of these polymers with that of PVK (Tg = 500°C) wherein the carbazole moiety is directly attached to the backbone chain, we observe a major decline. The conformational stiffness of the carbazole group results in a higher Tg. Thus, introduction of flexible spacers between main-chain and carbazole ring renders flexibility and prevents tight packing between polymeric main-chains. This leads to an increase of free volume in the homopolymer, PC leading to a lower Tg.

Table of Contents