

NMR, FLUORESCENCE AND THERMAL STUDIES OF N-VINYLCARBAZOLE COPOLYMERS

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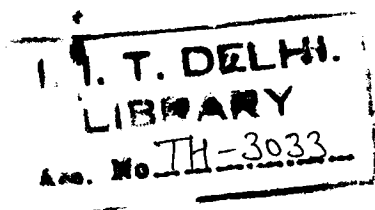
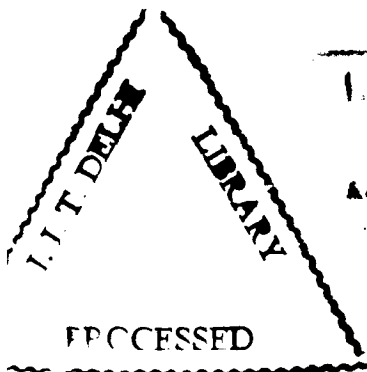
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*Submitted
in fulfilment of the requirements of the degree of*
DOCTOR OF PHILOSOPHY

to the



**INDIAN INSTITUTE OF TECHNOLOGY, DELHI
INDIA
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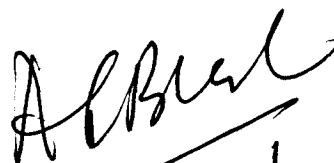
To

My Family

CERTIFICATE

This is to certify that the thesis entitled, "**NMR, FLUORESCENCE AND THERMAL STUDIES OF N-VINYLCARBAZOLE COPOLYMERS**", being submitted by Ms. Manpreet Kaur 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. Manpreet Kaur 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 works embodied in this 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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Manpreet Kaur
(Manpreet Kaur)

ABSTRACT

Poly(N-vinylcarbazole) (PVK) has attracted the attention of both polymer scientists and photophysicists mainly from two points. Firstly, PVK is the most sensitive photoconductive organic polymer and finds important applications in electrophotography and secondly it has distinctive ability to form different excimers by the interactions of the intramolecular carbazole moieties. However, due to the bulkiness of the pendant carbazole group, the polymer chains are stiff in nature and PVK is a brittle substance with poor mechanical and processing characteristics. Copolymerization with suitable monomers soften the resulting product leading to better film properties and improve its mechanical properties.

The properties of polymers are influenced by their molecular level microstructure that involves the sequence distribution and stereochemical arrangements of various monomer units in the polymer chain. The information obtained from microstructure can further be used to synthesize the copolymers with the desired physicochemical properties. It is well known that NMR spectroscopy is probably the most effective method for characterizing the microstructure of polymers.

The work embodied in this thesis deals with the synthesis and characterization of the copolymers of N-vinylcarbazole with monomers like vinyl acetate, methyl acrylate, methyl methacrylate, butyl acrylate and butyl methacrylate. Keeping in view the significance of the polymer microstructure, in this research work, we have determined the compositional and configurational sequences of these copolymers using one-dimensional (^1H , $^{13}\text{C}\{^1\text{H}\}$ and DEPT) and two-dimensional (HSQC, TOCSY) NMR techniques.

To a very large extent the practical utility of polymers depend upon their glass transition temperature. The knowledge of the variation of glass transition temperature of random copolymers with copolymer composition is important in order to control the glass transition of the final product. The dependence of the glass transition temperature on copolymer composition in these copolymers has been analyzed by using different theories that take into account the sequence distribution in the copolymer. Analysis of the thermal stability of these copolymers is also done.

PVK shows distinct excimer forming characteristics, besides the monomer carbazole fluorescence band, the fluorescence spectrum of PVK consists of two other fluorescence bands at about 370 and 420 nm, which arise from conformations with partial and total overlap, respectively of the two carbazole groups. To understand the spectral characteristics and the mechanism of the excimer formation, absorption, fluorescence and fluorescence excitation spectra and time dependent spectrofluorometric studies of these copolymers have been carried out.

The thesis is divided into five chapters. The **first chapter** describes the review of the literature, the general introduction about the microstructure of the polymers and the use of NMR spectroscopy for microstructure and sequence determination. This chapter also describes the general introduction about the fluorescence and the thermal studies of polymers.

The **second chapter** describes the experimental procedures followed for the preparation of homopolymers and copolymers of N-vinylcarbazole. This chapter includes the detailed description of all one and two-dimensional NMR, fluorescence and the thermal experiments carried out throughout this research work.

The **third chapter** describes with the NMR studies of the N-vinylcarbazole copolymers. The compositions of the copolymers are determined from $^{13}\text{C}\{^1\text{H}\}$ NMR spectra and their comonomer reactivity ratios are determined by Kelen Tudos (KT) and error in variables (EVM) methods.

In N-vinylcarbazole / vinyl acetate (V/A) copolymers, the methine regions of both A and V units show triad compositional sensitivity and the β -methylene region of these copolymers shows dyad compositional sensitivity. The various overlapped resonance signals in the ^1H NMR spectrum are assigned with the help of 2D HSQC NMR spectrum by one to one correlation between carbon and proton axis. The TOCSY spectrum helps to understand the connectivity between the different protons and confirms the various couplings in the polymer chain.

The methoxy region of the M unit and the methine region of V unit of N-vinylcarbazole / methyl acrylate copolymers (V/M) overlap in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The DEPT-90 NMR spectrum is recorded to separate them. The methine carbon resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR of both V and M units of the copolymer are sensitive to triad compositional sequences. The β -methylene group shows both compositional and configurational sensitivity. This region being complex and overlapped in both proton and $^{13}\text{C}\{^1\text{H}\}$ NMR has been assigned with the help of HSQC NMR spectra.

The carbonyl and methyl regions of M unit of N-vinylcarbazole / methyl methacrylate copolymers (V/M), are sensitive to triad compositional and configurational sequences. The methine region in V unit and the methoxy region of M unit are also sensitive to triad compositional sequences. The β -methylene region shows both

compositional and configurational sensitivity. This region is assigned to **MM**, **MV** and **VV** dyads by comparing change in intensity of the signals with change in the copolymer composition and the homopolymers. The **MV** dyad shows further splitting along both the carbon and the proton axis. The splitting along the carbon axis is divided into **MV** centered tetrad compositional sequences and along the proton axis, this region shows configurational sensitivity. The vicinal couplings between the methine protons in **V** centered triads with β -methylene protons in various dyads are assigned in the TOCSY spectra. The various assignments done are by comparing TOCSY NMR spectra of the copolymers of various compositions and those of the corresponding homopolymers.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of N-vinylcarbazole / butyl acrylate copolymers (**V/B**), the methylene carbon region of both **V** and **B** units and the methine carbon region of **B** unit are overlapped. These regions are separated with the help of DEPT-135 NMR spectrum and further these assignments are confirmed with the help of DEPT-90 NMR spectrum. The methine group in both **V** and **B** units show triad compositional sensitivity. The side-chain methylenes of **B** unit show triad compositional sensitivity. In the β -methylene region, the meso configuration of both **BB** and **BV** dyads give two crosspeaks due to two methylene protons and one crosspeak in between these two crosspeaks due to the racemic configuration. The vicinal couplings between the methine protons and methylene protons are assigned in the TOCSY spectra by comparing TOCSY spectra of the copolymers of various compositions and that of the corresponding homopolymers.

In the N-vinylcarbazole / butyl methacrylate copolymers (**V/B**), the carbonyl and methyl resonance signals of **B** unit are assigned to triad compositional and configurational sequences. The side chain methylene carbon resonance signals of **B** unit

as well as the methine carbon resonance signals of V unit are assigned to triad compositional sequences and the β -methylene carbon resonances of both V and B units are assigned to dyad and tetrad compositional and configurational sequences with the help of HSQC and TOCSY NMR spectra of various compositions of the copolymers.

The **fourth chapter** describes the fluorescence studies carried on these copolymers. The fluorescence excitation spectrum observed in each case and at different emission wavelengths resemble with each other and also with the respective absorption spectrum. This indicates that the precursor for all the different spectral characteristics of the first singlet state is the same i.e. only one kind of species is present in the ground state and the absorbing and emitting species are the same.

The fluorescence spectra of N-vinylcarbazole copolymers depend upon the N-vinylcarbazole content in them. At low carbazole content, the spectral features are similar to that of isolated carbazole moiety. This has been further substantiated by observing single exponential decay observed in the fluorescence decay profiles, with lifetime similar to that of isolated carbazole molecule (~ 8 ns). This confirms that carbazole moieties at low content are present at large distance and thus intramolecular overlap does not occur. The presence of the pendent methyl group in methyl and butyl acrylate which further hamper the overlap of the carbazole moieties due to the steric hindrance.

As the carbazole content in the copolymers increases, structure in the emission spectra gets diffused and the broadening of the spectrum occurs tending more towards red. This broadening is attributed to the emission from excimers. In the fluorescence decay profiles, the species with lifetimes ~ 3 ns and ~ 15 ns are observed. The species with the lifetime of ~ 3 ns is a monomeric species and leads to the formation of both the

excimers. The fluorescence decay profiles monitored at emission wavelength above 420 nm are composed of negative pre-exponential term having lifetime of ~ 3 ns and positive pre-exponential term with lifetime of ~ 15 ns. The negative amplitude of this species suggests that low energy excimer is formed from this species. There are two kinds of excited carbazole units, one with lifetime of ~ 3 ns leading to the formation of excimer and the other monomer with lifetime of ~ 8 ns which can not form excimers. The excimers are thus formed by the interaction of carbazole-carbazole overlap, present on the polymer chain and in contact with each other. The size and the number of the comonomers present in the N-vinylcarbazole copolymer chain, hinder the formation of the excimers due to the steric hindrance.

The **fifth chapter** deals with the thermal studies of N-vinylcarbazole copolymers. The dependence of the glass transition temperature on composition in these copolymers has been analyzed by using different theories that take into account the sequence distribution in the copolymer and these fit best the experimental data. Analysis of the thermal stability of these copolymers is also done which reveals high values of the degradation temperature even for samples with a low content in N-vinylcarbazole. Thus, the copolymerization of N-vinylcarbazole with these monomers allows to obtain copolymers with a lower glass transition temperature than PVK and are more processable while maintaining the same thermal stability.

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