

**SYNTHESIS AND CHARACTERIZATION OF  
CARBAZOLE BASED COPOLYMERS**

*by*

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DEPARTMENT OF CHEMISTRY**

*Submitted  
In fulfillment of the requirements of the degree of*

**DOCTOR OF PHILOSOPHY**

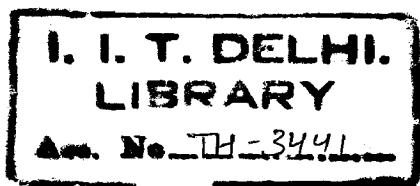
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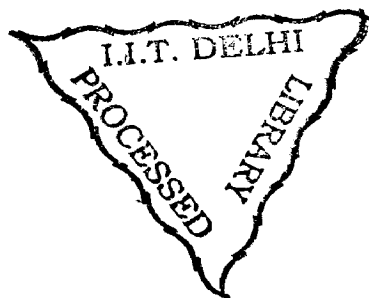
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Carbazole based Copolymers  
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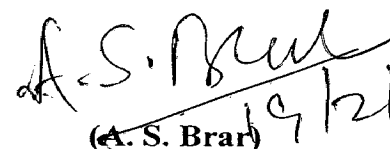
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## CERTIFICATE

This is to certify that the thesis entitled, “**SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE BASED COPOLYMERS**”, being submitted by Mr. Pravin Kumar Singh 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. Pravin Kumar Singh 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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**Dedicated**  
**to**  
**My Parents**

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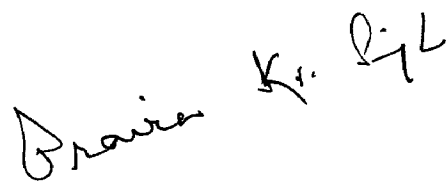
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Last, but not the least I would like to thank the almighty, without whose blessings, nothing would have been possible.

A handwritten signature in black ink, reading "Pravin K. Singh". The signature is written in a cursive style with a large initial 'P' and a stylized 'K'.

**(Pravin Kumar Singh)**

## **ABSTRACT**

Carbazole based polymers have created a class of its own in photosensitive/ photorefractive systems which are used in recording media for holographic storage and processing. Poly(N-vinylcarbazole) (PVK) is the simplest carbazole containing polymer and has been a topic of intensive research, as it is the most sensitive photoconductive organic polymer and have distinct ability to form different excimers. 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. Carbazole has been derivatized and carbazole containing monomers have been copolymerised with various monomers to achieve the desired properties such as to improve processability and film properties. It has been reported that it is ideal for the photorefractive polymers to possess a low glass transition temperature (T<sub>g</sub>) so that the 'orientation effect' of dipoles due to photo induced space charge field can be utilized to enhance the photorefractive performances. Low T<sub>g</sub> also allows easy preparation of thick films for holographic studies. It has also been reported that copolymerization greatly affects the T<sub>g</sub>. Thus, copolymerizations with suitable monomers soften the resulting product leading to better film and mechanical properties.

Free radical polymerization has been invariably used in industries as well as in research for the synthesis of polymeric materials due to its versatility. It is inexpensive, relatively simple, requires mild reaction conditions and is tolerant to impurities. There has also been a lot of research done to develop polymerization

technique that has control over molecular weight and is living in nature. Polymerization techniques such as anionic, cationic, etc are very selective towards monomers and solvents, and intolerant towards impurities. Recent years have witnessed the flourishing of controlled/living radical polymerizations (CRP's). These methods produce well-defined polymers with narrow molecular weight distributions and high degree of end functionalization. Thus it 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) is one of the most robust method within the spectrum of CRP processes as it is tolerant towards a wide range of monomers and solvents of different polarity.

To understand structure-property relationships at the molecular level, microstructure determination of polymers in solutions has been a topic of interest. It has been observed that the macroscopic (mechanical, thermal, optical or electrical) properties of polymers are critically dependent on the microstructure. Nuclear Magnetic Resonance (NMR) spectroscopy is probably the most powerful technique used in the determination of microstructure of polymers as chemical shifts are very much sensitive towards the change in configurational and/or compositional sequences. One-Dimensional (1D) NMR techniques have been very much useful in quantitative estimation of the polymers, but due to the complexity of  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of copolymers, complete assignments are not always an easy task. DEPT NMR technique has been used to distinguish various methyl, methylene and methine signals. Further, Two-Dimensional (2D) NMR methods have been

extensively used in the unambiguous assignments of  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of polymers. 2D Heteronuclear Single Quantum Coherence (HSQC) is an useful technique to get one to one correlation between carbon and attached protons. The Total Correlation Spectroscopy (TOCSY), with different mixing times, has been invariably used to understand the connectivity between the different protons and to confirm the various couplings in the polymer chain. While at low mixing time, one obtains the direct (two to three bond) coupling i.e the geminal and vicinal couplings, at high mixing time, one can obtain the relay (four to five bond) couplings through magnetization transfer as well. Moreover, long range carbon-proton couplings can be obtained from Heteronuclear Multiple Bond Correlation (HMBC) NMR technique. Thus it has often been used to make stereochemical and compositional assignments of quaternary carbons. Glass transition temperature ( $T_g$ ), which represents the molecular mobility of polymer chains, is an important phenomenon that influences the material properties and potential applications of a given polymer. The knowledge of variation in glass transition temperature of random copolymers with copolymer composition is important in order to control glass transition temperature of the final polymer. Likewise, it is important to know the thermal degradation temperature to ensure a safety service temperature, which is required to maintain their properties. These properties can be extremely affected by the presence of particular sequence of comonomers. Analysis of the thermal stability of these (co) polymers is also done.

The work embodied in this thesis deals with the synthesis and characterization of carbazole containing (co)polymers using free radical polymerization and ATRP.

Keeping in view the importance of polymer microstructure, we have also determined the configurational and compositional sequences of these copolymers using 1D and 2D NMR techniques.

The thesis consists of five chapters. **Chapter I** contains the review of literature related to carbazole and its (co)polymers, a brief introduction to various types of polymerization, significance of controlled radical polymerization, importance of Atom Transfer Radical Polymerization (ATRP) and a general introduction about the microstructure and the review of literature related to NMR of polymers. It also describes the use of 2D NMR spectroscopy (especially HSQC, TOCSY and HMBC) for microstructure determination. A general introduction to the different theories which correlate the glass transition temperature with copolymer composition and copolymer sequence distribution is also discussed in this chapter.

**Chapter II** includes the experimental details for the preparation of carbazole based monomer, “N-acryloylcarbazole”, its homopolymer and copolymers by free radical polymerization. It also includes experimental details for the preparation of copolymers of N-vinylcarbazole by atom transfer radical polymerization. Experimental details of the molecular weight determination by GPC are given. The composition of the copolymers was determined from  $^1\text{H}$  NMR spectrum. A description for all the 1D NMR ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and DEPT) and 2D NMR (HSQC, TOCSY and HMBC) experiments are incorporated. Experimental detail about the determination of glass transition temperature by Differential Scanning Calorimetry (DSC) and thermal degradation temperature by Thermogravimetric Analysis (TGA) is also given.

**Chapter III** deals with the microstructure and thermal analysis of N-acryloylcarbazole, poly(N-acryloylcarbazole) and N-acryloylcarbazole/methyl methacrylate copolymers. N-acryloylcarbazole was synthesized from carbazole in a two step synthesis which was then homopolymerized by free radical bulk polymerization to obtain poly(N-acryloylcarbazole). The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of N-acryloylcarbazole was unambiguously assigned with the help of DEPT-135, 2D HSQC and 2D TOCSY experiments. The poly(N-acryloylcarbazole) was found to be thermally stable. Moreover, the Tg of the poly(N-acryloylcarbazole) was found to be 430.4 K which is almost 155 K higher than its alkyl homologue (polyvinylketone) which indicates that the rigid carbazole ring hinders the rotation around the bond in the chain, but, at the same time, this value is about 70 K lower than poly(N-vinylcarbazole), which makes its mechanical property better than the latter. The copolymers of N-acryloylcarbazole with methyl methacrylate (A/M) were prepared by free radical solution polymerisation. The reactivity ratios of co-monomers in A/M copolymer system have been found to be  $r_A = 1.12 \pm 0.16$ ,  $r_M = 0.94 \pm 0.14$  and  $r_A = 1.05$ ,  $r_M = 0.90$  by KT and EVM methods, respectively. The methine carbon,  $\alpha$ -methyl carbon and carbonyl carbon resonances are assigned to triad compositional sequences, but quantitative calculations could not be done as signals obtained were very broad. The broadening is due to the restricted rotation of bulky carbazole moiety. The Complex  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of copolymers have been assigned with the help of HSQC and HMBC. The complex  $^{13}\text{C}$  NMR spectrum is resolved by the help of DEPT, HSQC and HMBC. The DSC studies are used to study

the rigidity of the chain. The value of  $T_g$  varies with the variation in copolymer composition. As the amount of N-acryloylcarbazole increases, the  $T_g$  increases from 378 K for poly(methyl methacrylate) to 430 K for poly(N-acryloylcarbazole). The dependence of the  $T_g$  on the composition of the copolymers is analyzed by using different theories that take into account the sequence distribution in the copolymer. The theoretical values obtained by these equations are found to be in good agreement with the experimental data. The A/M copolymers are also thermally stable as observed from TGA studies. Thus it can be concluded that the processability on copolymerization increases without compromising on thermal stability.

**Chapter IV** deals with the NMR studies of the N-acryloylcarbazole/vinyl acetate and N-acryloylcarbazole/methacrylonitrile copolymers. The composition of the copolymer was determined by  $^1\text{H}$  NMR spectrum. The comonomer reactivity ratios, determined by Kelen-Tudos (KT) and nonlinear error-in-variables (EVM) methods were  $r_A = 16.75 \pm 1.38$ ,  $r_V = 0.0153 \pm 0.0023$  and  $r_A = 16.36$ ,  $r_V = 0.0147$ , respectively, for A/V comonomer pair A/V comonomer pair and  $r_A = 1.27 \pm 0.13$ ,  $r_M = 0.69 \pm 0.06$  and  $r_A = 1.30$ ,  $r_M = 0.69$ , respectively, for A/V comonomer pair A/M comonomer pair. The complex  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of copolymers were assigned with the help of DEPT, HSQC and TOCSY. The methine and methylene signals in A/V copolymers have been found to be compositional and configurational sensitive, which has been well resolved with the help of HSQC and TOCSY. The  $\alpha$ -methyl carbon resonances of M unit are assigned to triad compositional sequences in A/M copolymers. The DSC studies are used to study the rigidity of the chain. The

value of  $T_g$  varies with the variation in copolymer composition.  $T_g$  increases with the amount of N-acryloylcarbazole. The dependence of the  $T_g$  on the composition of the copolymers is analyzed by using different theories that take into account the sequence distribution in the copolymer. The copolymers were found to be thermally stable.

**Chapter V** contains the details of copolymerization of N-vinylcarbazole/Ethyl methacrylate and N-vinylcarbazole/Ethyl acrylate copolymers by ATRP and their microstructure (NMR) and thermal analysis. Copolymerization of N-vinylcarbazole and ethyl methacrylate (V/E) using atom transfer radical polymerization (ATRP) was carried out under optimized reaction conditions using methyl 2-bromopropionate as initiator and CuBr/N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) as catalyst at 80 °C. Molecular weight distributions, determined by Gel Permeation Chromatography, showed linear increase in  $M_n$  with conversion indicating towards a controlled radical polymerization and low polydispersity ( $1.13 < M_w/M_n < 1.32$ ). Percentage conversion was determined gravimetrically. The copolymer composition was obtained from quantitative  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra. Due to the large difference in the reactivity ratios there has been a compositional drift in the copolymer composition with increase in conversion and the reactivity ratios determined by low conversion methods such as KT and EVM have been found to be erroneous. So, reactivity ratios were optimized using Mao Huglin equation and the value thus obtained was  $r_V = 0.80$  and  $r_E = 7.10$  for V/E comonomer pair and  $r_V = 0.067$  and  $r_A = 0.764$  for V/A comonomer pair. A complete spectral assignment has been done for the V/E and V/A copolymers, prepared by ATRP, with the correlation of 1D ( $^{13}\text{C}\{^1\text{H}\}$ , DEPT-135) and

2D (HSQC, HMBC) NMR spectroscopy. In V/E copolymers, the  $\alpha$ -methyl and carbonyl carbons have been found to be compositionally and configurationally sensitive and have been completely assigned with the help of HSQC, TOCSY and HMBC. The methine and methylene groups have been resolved with the help of HSQC spectrum. In V/A copolymers, the methine carbon of A unit was found to be compositionally sensitive and has been completely assigned with the help of HSQC and TOCSY. The DSC studies are used to study the rigidity of the chain. The value of  $T_g$  varies from 500K for poly(N-vinylcarbazole) to 339K for poly(ethyl methacrylate) and to 246K for poly(ethyl acrylate) with the variation in copolymer composition. The dependence of the  $T_g$  on the composition of the copolymers is analyzed by using different theories that take into account the sequence distribution in the copolymer.

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