

**NMR STUDIES OF ACRYLATE AND
METHACRYLATE COPOLYMERS**

by

SONIA GANDHI

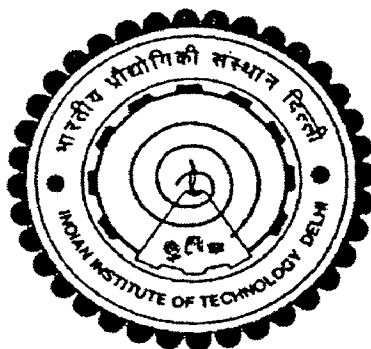
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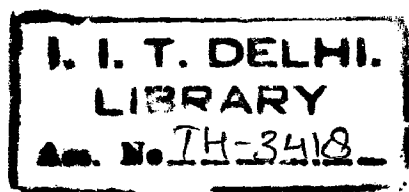
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NMR spectroscopy
Acrylate copolymers
Methacrylate copolymers



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**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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Sonia Gandhi
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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 with carbazole containing units.

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

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

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 copolymers. 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 of their processability, charge transport and thin-film making properties by having control over molecular weight, structure etc, which in turn could be achieved by ATRP polymerization. The crucial part played by NMR in determining the microstructure has been highlighted. Also the advantages of ATRP over conventional radical polymerization has been discussed which has been further used to synthesis block copolymers. The approach adopted in this research work along with its contribution to the field of polymers and NMR has been incorporated. Various aspects of solid-state spin diffusion NMR studies have been discussed. Also studies done and advantages of ^{13}C $T_{1\rho}$ measurements in the rotating frame to study the morphology of block copolymers have been dealt.

arious assignments in $^{13}\text{C}\{^1\text{H}\}$ NMR 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 good agreement between the two sets of 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 $-\text{OCH}_2$, $-\text{NCH}_2$ 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 (^1H , $^{13}\text{C}\{^1\text{H}\}$, 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. T_g for different compositions of E/A copolymers has been determined by DSC showing a decrease in T_g with decreasing E content due to increasing flexibility of the polymeric chain.

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

The experimental details for the various 1D (^1H , $^{13}\text{C}\{^1\text{H}\}$, 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 ^1H 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 overview of the synthesis of Styrene (S)/Methyl methacrylate (MMA) diblock copolymers via Atom Transfer Radical Polymerization (ATRP) has 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. Signal assignment to different carbon resonances were done using $^{13}\text{C}\{^1\text{H}\}$ NMR in conjunction 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 (^1H , $^{13}\text{C}\{^1\text{H}\}$ 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 $r_C = 0.31 \pm 0.03$, $r_N = 0.80 \pm 0.02$ and $r_C = 0.35$, $r_N = 0.83$ respectively. 1D (^1H , $^{13}\text{C}\{^1\text{H}\}$, 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 were assigned to dyad and triad configurational and compositional sequence respectively which were further strengthened by 2D HSQC and TOCSY experiments. The higher carbon/proton bond order couplings between nitrile carbon and α -methyl protons were studied by 2D HMBC NMR experiments.

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

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 $d_{\text{long}} \propto Mn^{2/3}$.

The molecular motions for ^{13}C in PS-*b*-PMMA have been measured using ^{13}C CP/MAS NMR technique. ^{13}C $T_{1\rho}$ spin-lattice relaxation times in the rotating frame were measured for aromatic and carbonyl carbons in the block copolymer. The results obtained showed biexponential decays, which in turn showed the presence of two phases in both rigid and mobile component. The $T_{1\rho}^{\text{short}}$ and $T_{1\rho}^{\text{long}}$ relaxation times were obtained for each component and their correlation with change in molecular weight of PS-*b*-PMMA was established and it was found that the study is on the fast side of $T_{1\rho}$ minimum. It was proposed that the morphology of PS-*b*-PMMA has rigid, interface and mobile component where the interface has contribution from both rigid and mobile component. Hence ^{13}C NMR has proved to be a very powerful technique for studying local dynamics in PS-*b*-PMMA polymer chains.

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