MULTIDIMENSIONAL NMR STUDIES OF TERPOLYMERS POLY(ETHYLENE-CO-VINYL ACETATE-CO-CARBON MONOXIDE) AND POLY(ETHYLENE-CO-1-HEXENE-CO-CARBON MONOXIDE)

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MULTIDIMENSIONAL NMR STUDIES OF TERPOLYMERS POLY(ETHYLENE-CO-VINYL ACETATE-CO-CARBON MONOXIDE) AND POLY(ETHYLENE-CO-1-HEXENE-CO-CARBON MONOXIDE)

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ABSTRACT

A series of poly(ethylene-co-vinyl acetate-co-carbon monoxide) (polyEVC) terpolymer samples with varying monomer compositions were studied using a variety of one- and two-dimensional nuclear magnetic resonance (NMR) techniques on a 750 MHz NMR instrument. NMR is one of the powerful techniques to study the microstructures of polymers. For a long time, one-dimensional (1D) NMR was used to identify polymer structures. Although useful for solving problems at initial stages, it can only help to approximate the assignment of resonances in complex polymers. In such cases, two-dimensional (2D) NMR can be used to disperse the resonances in a second dimension, thus solving overlap of resonances. The resonances can also be confirmed by correlation experiments. In the study of unlabeled polyEVC polymers 1D $^1$H and $^{13}$C NMR experiments were used for the primary assignment of resonances. The spectra were found to contain extreme overlap due to various combinations of resonances from the three monomers used in the polymer. To overcome this problem, 2D NMR experiments were used. 2D $^1$H/$^{13}$C heteronuclear single quantum correlation (HSQC), heteronuclear multiple-bond correlation (HMBC) and HSQC followed by total correlation (HSQC-TOCSY) experiments were used. These experiments not only helped to confirm the assigned resonances but were also useful to assign new resonances from low probability units. Thus, due to improved dispersion, the study was not just restricted to triad levels.
but in some cases assignment could also be done at the tetrad or pentad levels. It was also possible to identify and assign distinct resonances from chain-ends and short chain branches. In spite of the dispersion in 2D NMR, some regions of the spectra could not be assigned unambiguously. This is due to extreme overlap of resonances from large number of n-ads produced from the monomers and stereosequences. To circumvent this problem the study was continued using three-dimensional (3D) NMR experiments. The 3D experiments used so far needed a third NMR active X-nucleus; but most of the commercially used polymers lacked one. To study the polymers which are primarily hydrocarbon based and thus are deficient in a third NMR active X-nucleus, a new suite of 3D NMR experiments was introduced recently. These experiments require that at least the structures of interest had $^{13}$C enrichment. This allows treatment of the two carbon nuclei as two different NMR active centers which can be selectively excited at two different times and correlated in a 3D spectrum. This approach was recently tested and applied in the structural study of an ethylene based polymer which was labeled selectively at n-butyl acrylate positions. Here, the two 3D NMR experiments, gHCAC$_X$ and gHC$_AC_X$-HH-TOCSY, were used for the structure elucidation of a similar polymer of ethylene, vinyl acetate and carbon monoxide which was selectively labeled at the two adjacent olefinic carbons of vinyl acetate. The 3D experiments provided enormous spectral dispersion, permitting the resolution of vinyl acetate signals which showed a tremendous overlap in 2D spectra. The two complimentary experiments facilitated the identification and assignment of resonances up to the pentad level which could not even be identified from 2D NMR experiments. These experiments were further applied in the study of another terpolymer poly(ethylene-co-1-hexene-carbon monoxide) (polyEHC*)
which was selectively $^{13}$C enriched at ketone carbonyl position. The polymer was prepared with high concentrations of carbon monoxide (C) to achieve alternating polymer where C alternated with either ethylene (E) or 1-hexene (H). 1D proton/carbon and 2D HSQC/HMBC experiments were used initially to assign the resonances. HMBC experiment was not very useful here as it failed to separate correlations from different environments near carbonyl carbons. 3D NMR experiments were extremely useful here to obtain connectivity information in the polymer. Two different environments were identified around the ketone carbonyl carbon. With the aid of 3D NMR, it was possible to confirm the alternating nature of this polymer.
DEDICATION

To my parents
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CHAPTER I

INTRODUCTION

The structure of a polymer determines its physical and mechanical properties. To modify the properties of the polymers to achieve desired results a second monomer is often added. This process is called copolymerization. Varying the monomer composition in the polymer can thus help to modify the properties of the polymer in a desired fashion, e.g. copolymerization of styrene with 1, 3- butadiene (SBR) imparts flexibility. Increase in the vinyl acetate content in ethylene-vinyl acetate (EVA) (trade names: Elvax, Ultrathene) decreases crystallinity, increases impact and crack resistance, flexibility and adhesion to a variety of substrates. A copolymer of 1, 3-butadiene with acrylonitrile (nitrile rubber, NBR) is noted for its oil resistance

Poly(ethylene-co-vinyl acetate-co-carbon monoxide) (polyEVC) is one such commercial polymer which is used most often for polymer modification purposes. It is compounded with the other plastics to act as toughner and flexibilizer, due to its high tensile strength and tear resistance. The resulting polymer blends find applications in the electrical and automotive industries. They are used to prepare industrial footwear, athletic shoe soles, roofing membranes, industrial vinyl films and sheets in construction areas. The structure-property relationship of the polymer is in part dependent upon the monomer sequence distribution which is controlled by the polymerization process,
catalysts or initiators used and the proportions of monomers. Microstructural changes such as monomer sequence, tacticity and stereoregularity also have a significant effect on the properties of the polymer. To understand the properties of the polymers and to modify them in a rational way, it is necessary to study the mechanism of polymerization which is evident in the microstructures of the polymers prepared.

Nuclear magnetic resonance (NMR) spectroscopy has been decisively established as one of the most powerful tools for the study of a variety of molecules. It has played a key role in the expansion of the study of small organic molecules, drugs, proteins, supramolecular materials like dendrimers and macromolecules like polymers. The study of polymers using NMR has been successful due to the fact that the NMR chemical shifts are extremely sensitive to monomer- and stereosequence effects.

It would be instructive at this point to discuss briefly the basics of NMR and the different NMR experiments used for the characterization of this polymer. This is a phenomenon shown by isotopes of nuclei which possess magnetic moments. When the nucleus is placed in external static magnetic field it undergoes precession about the field. The magnetic moments of the nucleus aligns relative to the field in a discrete number of orientations (spin states). Nuclear magnetic resonance occurs when the nucleus changes its state spin state, driven by the absorption of energy. This energy is applied in the form of electromagnetic radiation (radiofrequency), whose frequency must match the precession frequency (Larmor frequency) of the nucleus for the resonances to occur.

NMR experiments are most commonly performed by application of a series of radiofrequency pulses (pulse sequence) to manipulate nuclear spins to provide the desired information. Thus, in a simplest of the NMR experiment such as a one-dimensional (1D)
experiment, a single pulse is applied for a definite amount of time followed by emission of a time-domain, radiofrequency signal called the free-induction decay (FID) which is recorded and converted into frequency-domain signal by the Fourier transformation process. Some other 1D experiments such as APT\textsuperscript{7}, INEPT\textsuperscript{8}, and DEPT\textsuperscript{9} use complex pulse sequences.

The 1D pulse sequences can be subdivided into two units: preparation and detection. During the preparation period the spins are manipulated as desired; this is followed by the detection period when the signal generated is recorded. For example, a 1D one-pulse experiment has a relaxation time followed by a 90 degree pulse in the preparation period. During the relaxation time the nuclear spins align along the z-axis. After the application of a 90 degree pulse, generally along x-axis, the spins are rotated on the y-axis. This is followed by the detection period during which signal induced can be recorded, the spins precesses with its Larmor frequency around z-axis and returns to z-axis (relaxation). The relaxation of signal takes place by two processes: longitudinal relaxation ($T_1$) and transverse relaxation ($T_2$). As the signal obtained is in the absence of any radio frequency field and decays in an exponential form due to the relaxation processes it is called the free-induction decay (FID). The sequence is repeated numerous times and summed such that signal averaging produces a strong signal. This is followed by Fourier transformation to convert it into to the frequency domain signal.

To correlate the resonances of two nuclei in a molecule two-dimensional (2D) NMR can be used. Two-dimensions here refer to two frequency dimensions. All the 2D NMR experiments have the same basic format and can be subdivided into four units: preparation, evolution, mixing and detection. Analogous to the 1D experiment, the
preparation period usually comprises of a delay during which the spins are allowed to return to equilibrium; this is followed by a pulse or a cluster of pulses which places the equilibrium magnetization in the transverse plane, just before the evolution period. The evolution period \( t_1 \) is a variable time delay, and provides the key to the generation of the second dimension. The mixing period again consists of a pulse or pulses, during which the magnetization is transferred from one nucleus to another. The detection \( t_2 \) process involves collection of the data; this process is similar to the one in 1D experiments. The general scheme for any 2D experiment is shown below:

\[
\text{Preparation} \quad \rightarrow \quad \text{Evolution} (t_1) \quad \rightarrow \quad \text{Mixing} \quad \rightarrow \quad \text{Detection} (t_2)
\]

The evolution time, \( t_1 \), is a variable time delay which is increased in a stepwise manner from an initial value of zero to a final value of \( m \) (controlled by \( n_i \) in the 2D experimental parameters). For each value of \( m \) the 2D sequence is repeated \( n \) number of times (controlled by \( n_t \) in the 2D experimental parameters) and the data (FID) is stored with a \( p \) number of digitized data points (controlled by \( n_p \) in the 2D experimental parameters). As the \( t_1 \) delay increases the magnetization in the transverse plane is allowed to evolve for longer and longer time and the effect of this is observed on the amplitude modulation of the FIDs collected during the detection period \( t_2 \). Fourier transformation of all these FIDs with respect to \( t_2 \) produces a series of spectra containing resonances whose intensity (amplitude) varies as a function of time \( t_1 \) and can be plotted along \( f_2 \) frequency dimension in a 2D spectrum. The intensity of resonances as a function of time represents another set of free-induction decays that has been generated artificially. Subjecting these time domain data to Fourier transformation with respect to \( t_1 \) produces resonances which can be plotted along \( f_1 \) frequency dimension. Thus, repeated acquisition
of FIDs with systematically incremented $t_1$ time periods is fundamental to the generation of all two-dimensional data sets. Using the above theory two basic types of experiments can be used, homonuclear correlation experiments: which correlate two like spins and heteronuclear correlation experiments: which correlate different spins. Typical examples of homonuclear experiments are, correlation spectroscopy (COSY)\textsuperscript{10}, total correlation spectroscopy (TOCSY)\textsuperscript{11}, nuclear Overhauser effect spectroscopy (NOESY)\textsuperscript{12}. While the examples of heteronuclear experiments are, heteronuclear correlation spectroscopy (HETCOR)\textsuperscript{13}, heteronuclear multiple-quantum correlation (HMQC)\textsuperscript{14}, heteronuclear single-quantum correlation (HSQC)\textsuperscript{15}, heteronuclear multiple-bond correlation (HMBC)\textsuperscript{16}.

This simple idea of generating two-dimensions can be extended to produce a third-dimensional spectrum simply by having three independently incremented time periods, one detected ‘directly’ and two ‘indirectly’. Thus, a 3D pulse sequence consists of a preparation period, two evolution periods of time $t_1$ and $t_2$, two mixing periods, and a detection period at the end of length $t_3$. Fourier transformation with respect to $t_1$, $t_2$ and $t_3$ builds the three frequency dimensions, $f_1$, $f_2$ and $f_3$, respectively, in a 3D spectrum.

NMR spectroscopy has emerged as one of the most important methods for polymer characterization. It is a method of great interest and importance for the observation of every aspect of structure and properties of these macromolecules. It has played a key role in characterizing polymer microstructures and in the understanding of polymerization processes. 1D NMR, especially $^1$H and $^{13}$C NMR, has been used for decades for the characterization of polymers mainly due to this fact that most of the polymers have a majority of these atoms in the chain. However, $^1$H spectra show broader
lines due to small chemical shift separation for various microstructures. Hence, $^{13}$C NMR has been the most desirable tool for interpretation of structures in polymers. It gives relatively, well resolved lines for unique structures in a polymer and shows sensitivity towards repeat units. It is one of the most important tools for quantitative analysis, comonomer sequence distribution, and end-group analysis. In spite of these advantages, $^{13}$C NMR spectra have also been found to be complicated, especially to establish the assignment of stereosequences or for the polymers with two or three different monomers$^{17}$. Conditions can be sometimes be improved by raising the temperature or changing solvents.

To study polymer structures and to modify them to alter the properties, it is necessary to identify all the possible structural variations in the polymer. This can, in a predictable way, only be done by assigning the resonances to a specific structure or sequence. 2D NMR has proved to be an extremely useful tool for establishing the resonance assignments in polymers. This is due to the dispersion of overlapping resonances in a second dimension. Various 2D homo- and heteronuclear experiments can be used for the interpretation. 2D COSY$^{18}$ has been applied to assign the resonances from monomer sequences at the triad level in various ethylene containing co-and ter-polymers, while Beshah$^{19}$ applied a more recent technique, 2D HSQC-TOCSY, for the assignment of resonances in ethylene-vinyl acetate copolymer. The use of high field spectrometers and pulse field gradients (PFG)$^{20}$ has made 2D a powerful tool in the analysis of polymers. Application of PFG in 2D NMR experiments help in the selection of desired resonances presenting a cleaner spectrum, and also reduces the dynamic range problem. The use of PFG assisted 2D NMR experiments has been illustrated to study ethylene/1-
hexene/1-butene copolymers\textsuperscript{21}. To further simplify the resonances, the spectra were recorded at high temperature.

Combination of two or more 2D NMR experiments has become a regular practice for the structure elucidation in polymers. Sahoo \textit{et al.}\textsuperscript{22} used 2D gHSQC and gHMBC NMR experiments for the study ethylene-co-butene copolymer. 2D experiments such as gHSQC, gHMBC and gHSQC-TOCSY have also been very efficiently applied in the identification of short-chain branching resonances in a variety of ethylene copolymers\textsuperscript{23}.

As the number of monomers increase in the polymer, the NMR spectra become more complicated and the overlap of resonances increases due to the various combinations of monomer sequences. Unambiguous assignment of individual resonances often becomes an arduous task using established methods. 3D NMR for the study of polymers is a more recent technique. The need to disperse the complicated resonances further in the third-dimension has given rise to the 3D NMR experiments. Triple-resonance $^1$H/$^{13}$C/X 3D NMR experiments have been used in the past for the structure elucidation of synthetic polymers\textsuperscript{24}. These polymers contained a third NMR active nucleus such as $^{19}$F, $^{29}$Si, $^{31}$P, $^{119}$Sn which was essential for the experiments to be successful. These experiments were extremely useful in the structural assignment of carbosilane dendrimers\textsuperscript{25}, to characterize structures from chain-end functionalized poly(dimethylsiloxane) macromonomers\textsuperscript{26}, to study the structures of tri-n-butyline-capped polybutadienes\textsuperscript{27}. Although these 3D experiments were extremely effective in the study of the above mentioned polymers, they cannot be applied to the study of majority of commercial polymers. Most of the commercial polymers are hydrocarbons and lack a
third NMR active nucleus. To circumvent this problem a new suite of 3D NMR experiments, gHCA\textsubscript{X} and gHCA\textsubscript{X}-HH-TOCSY was introduced recently\textsuperscript{28}.

The new 3D NMR methods are designed for the characterization of hydrocarbon based polymers. For the experiments to be successful, \textsuperscript{13}C labeling of the polymer at a desired position is preferred. The methodology involves selective excitation of the resonances from the labeled sites as if they were from a third NMR-active X-nucleus. Two 3D experiments are used as complimentary experiments; the gHCA\textsubscript{X} experiment, which gives the connectivity between \textsuperscript{1}H\textsubscript{A}–\textsuperscript{13}C\textsubscript{A}–\textsuperscript{13}C\textsubscript{X}, and the gHCA\textsubscript{X}-HH-TOCSY experiment, which in addition to the HCA\textsubscript{X} correlations gives correlation from the \textsuperscript{1}H\textsubscript{A} resonances to the resonances of the neighboring protons in the spin system. These experiments can be applied to obtain complete atomic connectivity of the desired structural fragment.

The successful application of these experiments was first illustrated in the characterization of a variety of \textsuperscript{13}C labeled poly(ethylene-\textit{co}-1,2,3-\textsuperscript{13}C\textsubscript{3}-n-butyl acrylate-\textit{co}-carbon monoxide) where the carbon atoms of \textit{n}-butyl acrylate were labeled at different positions\textsuperscript{29}. The experiments illustrated the ability to disperse the resonances further in third dimension so that the complex resonances from B-centered structures could be identified and assigned. These experiments were particularly useful in the identification of low-concentration \textit{n}-butyl acrylate-carbon monoxide structures.

The study of copolymers of ethylene (E) and vinyl acetate (V) or ethylene and carbon monoxide (C) has been described in the past several years\textsuperscript{30-35}. This is due to the commercial significance of these polymers in diverse fields. This present work reports
the structure elucidation of terpolymers of ethylene with vinyl acetate and carbon monoxide using a variety of 1D, 2D and 3D NMR methods.

A range of commercial poly(ethylene-co-vinyl acetate-co-carbon monoxide) (polyEVC) with varying monomer compositions were studied. The 1D $^1$H and $^{13}$C NMR spectra of these polymers were found to be extremely complex. This is due to the overlap of resonances from various monomer sequences. The spectra have become more complex due to the additional resonances from the stereosequences, since the V unit introduces stereogenic centers in the polymer chain. Due to the complexity in the 1D spectrum only the major resonances could be assigned at triad levels and 2D NMR was used for further interpretations. 2D gHSQC experiment was used in order to establish one-bond proton-carbon correlations. The experiment was useful not only to obtain one-bond correlations but avoided the use of DEPT experiment to separate methylene from methyl and methine groups. To confirm the neighboring groups gHMBC and gHSQC-TOCSY experiments were used. gHSQC-TOCSY was very useful in some cases to assign the resonances unambiguously, when the gHMBC failed to show many correlations, possibly because of low concentrations of that particular triad sequence or due to cancellation of antiphase multiplet components.$^{36}$

2D NMR experiments were thus useful to confirm most of the possible triad sequences assigned by 1D experiments of polyEVC. The resonances also showed fine structure due to the effect of neighboring groups and in some cases it was possible to assign those resonances up to tetrad and pentad levels. Some minor resonances like those formed from V-C additions could also be identified using 2D NMR. The polymer also showed structures due to chain-end and short chain branch (SCB) formations. These
structures make the spectra more complicated. Some of the chain-end structures and SCB structures were identified in the 2D spectra of these polymers. However, the spectral complexity was still observed in some of the areas of the spectra. The spectra were found to be extremely complex due to overlapping resonances, especially due to structures in the methylene region, from groups which were one bond away from the methine groups of the vinyl acetate. Also the methine resonances showed a lot of overlap. Due to this, only a few resonances from the triads could be assigned in this area. Although, it was possible to confirm the \( m \)- and \( r \)- structures in the methine resonance regions. To solve this problem the two 3D NMR experiments mentioned earlier were used. As the structural assignment in the vinyl acetate region was more problematic, a polymer synthesized similar to the commercial polymers was used which was \(^{13}\)C enriched at the two polymer backbone carbons of vinyl acetate units. Thus, only one-third of the structures from V-centered n-ads were studied using 3D NMR methods. This approach simplified the problem tremendously as only desired structures were enhanced and selected by 3D NMR approach. Here, application of 3D NMR methods to solve yet another complex structural problem is demonstrated. The structures in the labeled polymer are identified here and assigned up to pentad levels using 3D NMR.
2.1 Synthesis of Polymers

Both the labeled and unlabeled polymers were synthesized by free-radical polymerization. Four samples, A, B, C and D, of unlabeled polymer samples with varying monomer compositions were synthesized while the labeled sample was synthesized with composition similar to sample C. The detailed process for the synthesis of both, the labeled and unlabeled samples is given below.

2.1.1 Synthesis of Unlabeled Poly(ethylene-co-vinyl acetate-co-carbon monoxide)

Four samples of the terpolymer, A, B, C and D were synthesized at E. I. duPont de Nemours and Co. The details of which are given below.

The terpolymers were prepared by free-radical polymerization using ethylene obtained from Sun, carbon monoxide from Messer/MG and vinyl acetate from Celanese. The reaction was initiated via thermal decomposition of organic peroxides. Samples were produced with a flow-through stirred autoclave pilot-plant reactor using high temperature (150-300 °C) and pressure (15-40 kpsi) reaction conditions. The produced polymer samples were degassed in a polymer separator, fed to a melt pump, and strand cut when
feasible. The monomer composition (mol %) of the polymers were determined by 1D $^{13}$C NMR.

2.1.2 Synthesis of Labeled Poly(ethylene-co-vinyl acetate-co-carbon monoxide)

The terpolymer was synthesized at Institut für Physikalische Chemie, Universität Göttingen by Dr. Michael Buback and Henning Latz. The procedure for preparation of the $^{13}$C enriched polymer provided is described here for completeness.

The $^{13}$C enriched poly(EV$_{\text{C}}$) was prepared from minimum 99% 1-2-$^{13}$C$_2$-vinyl acetate ($^{13}$CH$_2$=CH-OCOCH$_3$). A gaseous mixture of ethene (E) and carbon monoxide (C) was allowed to mix with a mixture of liquid vinyl acetate (V) and initiator (di-tert-butyl peroxide in heptane) in a syringe pump in an oxygen free environment. The pressure in the pump was maintained at 3000 bar for at least one day to ensure complete homogeneity. The mixture was then released into the reaction cell which was heated to 190°C in advance. The reaction pressure was maintained up to 2000 bar. The conversion was achieved in about 2-5 minutes. The synthesized polymer obtained after the reaction cell was cooled fast to room temperature and vacuum dried for up to 14 days. The conversion was calculated by gravimetric analysis and the composition was calculated from $^1$H NMR data.

2.2 Preparation of Polymers for NMR Analysis

The NMR spectra of the synthesized polymers was obtained in solution state hence a solution of the polymer samples was prepared using a deuterated solvent. The detailed process for the preparation of unlabeled and labeled samples in described below.
2.2.1 Preparation of Unlabeled Poly(ethylene-co-vinyl acetate-co-carbon monoxide) Samples for NMR Analysis

All the samples were dissolved in 1,4- dichlorobenzene-d$_4$ to produce ca. 8.5% (w/v) polymer solutions. The samples were heated to 120 °C and rotated at 20 rpm in a Kugelrohr oven for three to five hours to homogenize the solutions. Hexamethyldisiloxane (HMDS) was added in trace quantity to serve as an internal chemical shift reference in both the 1D and 2D NMR spectra (\(\delta_H = 0.09\) ppm, \(\delta_C = 2.00\) ppm).

2.2.2 Purification and Preparation of Labeled Poly(ethylene-co-vinyl acetate-co-carbon monoxide) Samples for NMR Analysis

The labeled polymer sample provided was found to be contaminated with magnetic substances hence a purification process was required before a sample could be prepared for NMR experiments.

The polymer sample was allowed to dissolve in a small amount of distilled methylene chloride at room temperature. This mixture was then filtered in the presence of a strong horse-shoe magnet (0.464T) to eliminate the magnetic impurities. The polymer was then vacuum dried to remove methylene chloride completely for two days before a sample for NMR analysis was prepared.

As the amount of purified sample was reduced by the purification process, hence, to increase the concentration, the sample was prepared in a 3mm tube. The sample was prepared by dissolving the purified polymer in 1, 4-dichlorobenzene-d$_4$ at 120 °C to produce ca. 2% (w/v) polymer solution. To obtain a homogeneous solution the sample
was rotated at 20 rpm in a Kugelrohr oven at the mentioned temperature for one to two hours. Hexamethyldisiloxane (HMDS) served as an internal chemical shift reference in the NMR spectra ($\delta_H = 0.09$ ppm, $\delta_C=2.00$ ppm).

2.3 Acquisition of NMR Spectra

All the NMR experiments were performed on Varian INOVA 750 MHz NMR spectrometer equipped with four radio-frequency channels and a Perform-II pulse field gradient accessory. The 1D $^1$H and $^{13}$C experiments were obtained using an H/X broadband (BB) 10mm probe. The 2D and 3D experiments were acquired using a Nalorac $^1$H/$^2$H/$^{13}$C/$^{15}$N 5mm PFG probe. All the NMR experiments were performed at 120 °C and the data were processed with Varian’s VNMR software on a SUN workstation.

2.3.1 Acquisition of 1D NMR Spectra

Quantitative $^{13}$C NMR experiments were performed on the four unlabeled polymer samples (A, B, C, and D). Spectra were acquired with the following parameters: a $\pi/2$ pulse of 11.1 $\mu$s; 47.2 kHz spectral width; 1024 transients, 1.35 s acquisition time and a 30 s relaxation delay for quantitative analysis. Spectra were obtained using WALTZ-16$^{37}$ gated decoupling to suppress the nuclear Overhauser effect (NOE); 128k data points were acquired for each fid and then the data were zero filled to 256 k and exponentially weighted with 0.5 Hz line-broadening before Fourier transformation.

The 1D $^{13}$C NMR spectrum of the labeled sample was obtained using a 5 mm broadband probe ($^{15}$N-$^{31}$P) on the same spectrometer. Spectra were acquired with the following parameters: a $\pi/2$ pulse of 11.9 $\mu$s; 47.1 kHz spectral width; 3072 transients,
1.39 s acquisition time and a 30 s relaxation delay for quantitative analysis. This spectrum was also obtained using WALTZ-16 gated decoupling; the data were zero filled to 256 k and exponentially weighted with 5 Hz line-broadening before Fourier transformation.

2.3.2 Acquisition of 2D NMR Spectra

Various 2D one-bond and long range heteronuclear experiments were used for the interpretation of the labeled and unlabeled polymer samples. For the resonance assignments of unlabeled polymers, 2D gHSQC, gHMBC and gHSQC-TOCSY were used. The labeled polymer was $^{13}$C enriched at the two adjacent carbons of the vinyl acetate. Due to which, the $^{13}$C-$^{13}$C (J_{CC}) coupling was observed along the $f_1$ dimension in the gHSQC spectrum. To avoid the complication of the spectra due to J_{CC} coupling, the constant evolution time (CT) $^{38}$ version of gHSQC was used to obtain one-bond proton-carbon correlations. gHMBC and gHSQC-TOCSY were also used in the interpretation of the data from the labeled sample.

2.3.2.1 Acquisition of 2D gHSQC and CT-gHSQC NMR Spectra

Gradient selected phase-sensitive HSQC (gHSQC) spectra were collected on the same spectrometer. The $\pi/2$ pulse widths for $^1$H and $^{13}$C were 10.3 $\mu$s and 15.0 $\mu$s, respectively. Data were acquired using the following parameters: relaxation delay 1 s, the delay $\Delta$ set to $1/(2 \times J_{CH})$, ($^1J_{CH} = 135$ Hz) to optimize the intensities of cross-peaks from one bond $^1$H-$^{13}$C correlations, and an acquisition time of 0.205 s with simultaneous $^{13}$C GARPI$^{39}$ decoupling; 24 transients were averaged for each of $2 \times 1024$ increments during
$t_1$ for phase sensitive detection based on the States method$^{40}$. The evolution time was incremented to provide the equivalent of a 17.36 kHz spectral window in the $f_1$ dimension and a 5.0 kHz spectral window was used in the $f_2$ dimension. The encoding and the decoding gradient pulses were 0.219 T/m and 0.109 T/m, with 2.0 ms and 1.0 ms durations, respectively. Linear prediction$^{41}$ was used to forward extend the data two- to four-times its original length, to compensate for the short acquisition time as well as the relatively small number of points sampled in the evolution time dimension. Data were zero filled to provide an $8192 \times 16384$ matrix and processed with sinebell and shifted sinebell weighting functions before Fourier transformation. The pulse sequence of gHSQC experiment is shown in Figure 2.1.

![Figure 2.1. Pulse sequence for the gHSQC experiment](image)

The CT-HSQC of the labeled sample was collected in the following manner: the $\pi/2$ pulse widths for $^1$H and $^{13}$C were 8.7 $\mu$s and 15.0 $\mu$s, respectively. Acquisition parameters were as follows: relaxation delay 1 s, the delay $\Delta$ set to $1/(2 \times ^1J_{CH})$, ($^1J_{CH} =$135 Hz) for one bond $^1$H-$^{13}$C correlations, constant evolution delay of 27 ms (based on $(n \times ^1J_{CC})^1$, where $n =$ integer), and an acquisition time of 0.109 s with simultaneous $^{13}$C GARP1 decoupling; 32 transients were averaged for each of $2 \times 352$ increments during $t_1$. 

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for phase sensitive detection with spectral width of 6.5 kHz in $f_2$ and 15.1 kHz in $f_1$ dimension. The two coherence selection pulses were 0.279 T/m and 0.276 T/m, with 1.6 ms and 0.4 ms durations, respectively. Linear prediction was used to forward extend the data two- to four-times its original length. Data were zero filled to provide a $4096 \times 8192$ matrix and processed with sinebell and shifted sinebell weighting functions before Fourier transformation. The pulse sequence of CT-HSQC is shown in Figure 2.2.

![Pulse sequence for the CT-gHSQC experiment.](image)

2.3.2.2 Acquisition of 2D gHMBC NMR Spectra

HMBC spectra of all the four unlabeled polymers were acquired using same parameters. Two sets of data were acquired with different $\tau$ delays of 50.0 and 100.0 ms (set to $1/ (2 \times J_{CH})$) to obtain two separate spectra with delays optimized for two- and three-bond $^{1}H$-$^{13}C$ correlations, a relaxation delay of 1.0 s, a 1.025 s acquisition time, a delay $\Delta_1$ set to $1/ (2 \times J_{CH})$ ($J_{CH} =135$ Hz) for suppressing the 1-bond $^{1}H$-$^{13}C$ correlations. Two spectra were recorded for each $\tau$ delay, with the $^{13}C$ transmitter centered in the aliphatic and carbonyl regions of the $f_1$ dimensions. The $^{1}H$ and $^{13}C$ $\pi/2$ pulse widths used
to obtain the spectra of the $^{13}$C aliphatic region were 10.3μs and 15μs, respectively. To obtain the spectra of the $^{13}$C carbonyl region, selective excitation with a 30μs $^{13}$C $\pi/2$ pulse width was used. The coherence selection between $^1$H and $^{13}$C was achieved using two 2.0 ms gradient pulses with strengths of 0.219 T/m and 0.164 T/m; 16 transients were averaged for each of 768 $t_1$ increments. The evolution time was incremented to provide the equivalent of 15.5 kHz spectral widths in the $f_1$ dimensions and 5.9 kHz spectral width in the $f_2$ dimensions. Data were zero filled to provide a $4096 \times 8192$ matrix and processed with sinebell and shifted sinebell weighting functions before Fourier transformation.

HMBC spectra of the labeled sample was acquired in the following manner: two sets of data were recorded for $\tau$ delay of 80.0 ms (set to $1/ (2 \times J_{CH})$), with the $^{13}$C transmitter centered in the aliphatic and carbonyl regions of the $f_1$ dimensions were acquired to obtain two- to three-bond $^1$H-$^{13}$C correlations. The following parameters were used to collect both the data sets: a relaxation delay of 1.0 s, a 0.159 s acquisition time, a delay $\Delta$ set to $1/ (2 \times J_{CH})$ ($J_{CH}$=135 Hz) for suppressing the 1-bond $^1$H-$^{13}$C correlations. The $^1$H and $^{13}$C $\pi/2$ pulse widths used to obtain the spectra of the $^{13}$C aliphatic region were 8.75μs and 15μs, respectively. To obtain the spectra of the $^{13}$C carbonyl region, selective excitation with a 30μs $^{13}$C $\pi/2$ pulse width was used. The coherence selection was achieved using two 2.0 ms gradient pulses with strengths of 0.214 T/m and 0.108 T/m; 32 transients were averaged for each of 1408 $t_1$ increments. The evolution time was incremented to provide the equivalent of 15.5 kHz spectral width in the $f_1$ dimensions and a 6.5 kHz spectral width in the $f_2$ dimensions. Data were zero filled to provide a $4096 \times$
8192 matrix and processed with sinebell and shifted sinebell weighting functions before Fourier transformation.

The pulse sequence used to obtain HMBC data of unlabeled and labeled samples is shown in Figure 2.3.

Figure 2.3. Pulse sequence for the gHMBC experiment.

2.3.2.3 Acquisition of 2D gHSQC-TOCSY NMR Spectra

The gradient selected, phase-sensitive HSQC-TOCSY of the four unlabeled samples were obtained using following parameters: $\pi/2$ pulse widths for $^1$H and $^{13}$C were 10.0 $\mu$s and 14.5 $\mu$s, respectively, a 1s relaxation delay, a delay $\Delta$ set to $1/(2 \times ^1J_{CH})$, ($^1J_{CH} = 135$ Hz) for optimizing the intensities of cross-peaks from one bond $^1$H-$^{13}$C correlations, a 40 ms MLEV-17$^{42}$ spin lock period with an 8.9 KHz spin lock field, and a 0.182s acquisition time with $^{13}$C GARP1 decoupling; 24 transients were averaged for each of $2 \times 1024$ $t_1$ increments. The 2 ms and 1 ms coherence selective gradients between $^1$H and $^{13}$C were of 0.219 T/m and 0.110 T/m strengths, respectively. Data were zero filled to provide a 4096 $\times$ 4096 matrix and processed with sinebell and shifted sinebell weighting functions before Fourier transformation.
HSQC-TOCSY spectrum of labeled sample was acquired using following parameters: \(\pi/2\) pulse widths for \(^1\text{H}\) and \(^{13}\text{C}\) were 8.8\(\mu\text{s}\) and 15\(\mu\text{s}\), respectively, a 1s relaxation delay, a delay \(\Delta\) set to \(1/(2 \times ^{1}\text{J}_{\text{CH}})\), \(^{1}\text{J}_{\text{CH}} = 135\ \text{Hz}\) for one bond \(^{1}\text{H}-^{13}\text{C}\) correlations, a 40 ms MLEV-17 spin lock period with an 8.0 KHz spin lock field, and a 0.15 s acquisition time with \(^{13}\text{C}\) GARP1 decoupling; 24 transients were averaged for each of \(2 \times 1152 \times t_1\) increments. The coherence selective gradients were of 0.214 T/m and 0.107 T/m strengths for 2 ms and 1 ms, respectively. Data were zero filled to provide a \(4096 \times 4096\) matrix and processed with sinebell and shifted sinebell weighting functions before Fourier transformation.

The pulse sequence used to obtain HSQC-TOCSY data of unlabeled and labeled samples is shown in Figure 2.4.

![Figure 2.4. Pulse sequence for the HSQC-TOCSY experiment.](image)

2.3.3 Acquisition of 3D NMR Spectra

The 3D analysis of labeled sample was conducted using two 3D NMR experiments: \(g\text{HC}_A\text{C}_X\) and \(g\text{HC}_A\text{C}_X\text{-HH-TOCSY}\). The 3D spectra were collected using the two channel version of the pulse sequences.
2.3.3.1 Acquisition of 3D gHC\textsubscript{A}C\textsubscript{X} NMR Spectra

The 3D gHC\textsubscript{A}C\textsubscript{X} NMR spectrum was collected using the two channel version of the pulse sequence. The \(\pi/2\) pulses for \(^1\text{H}\) and \(^{13}\text{C}\) were 8.8\(\mu\text{s}\) and 15\(\mu\text{s}\), respectively. The spectral width of 1131.2, 1884.3 and 5549.8 were used along \(f_1\), \(f_2\) and \(f_3\) dimensions. The spectra were acquired using following acquisition parameters: a relaxation delay of 1s, a delay \(\Delta\) of 2.0 ms (1/4\(J_{\text{CH}}\), where \(J_{\text{CH}} = 135\text{Hz}\)), a delay \(\tau_1\) of 3.0 ms (1/8\(J_{\text{CC}}\), where \(J_{\text{CC}} = 40\text{Hz}\)) and a constant evolution time delay \(T\) of 6.0 ms (1/4\(J_{\text{CC}}\), where \(J_{\text{CC}} = 40\text{Hz}\)) to enhance the minor signals from VV units followed by a 0.13s of acquisition time with GARPI decoupling; 32 transients were averaged for each of \(2 \times 24\) increments during \(t_1\), \(2 \times 20\) increments during \(t_2\), and a total of 1408 points in \(t_3\). The off-resonance selective excitation of the methine carbon region (37 ppm away from the carbon transmitter) was achieved by a shifted laminar pulse\textsuperscript{43} which was created by setting the carbon transmitter at 35.69 ppm and then by using the “make180C_CO” macro in Varian’s ProteinPack software. The selective \(\pi/2\) \(^{13}\text{C}\) pulses were calculated using the formula: \(\sqrt{15/4 \times \text{dfrq (Hz)} \times (\text{offset difference between aliphatic (35.69 ppm) and methine (72.69 ppm) regions})}\), where \(\text{dfrq}\) is the \(^{13}\text{C}\) decoupler frequency. To decouple the protons during the transfer of magnetization from \(C_A\) to \(C_X\), \(t_1\) evolution and during the constant time period, WALTZ-16 decoupling with \(\gamma B_1 = 7.5\ \text{kHz}\) was used. The \(^1\text{H}-^{13}\text{C}\) coherence transfer was accomplished by \(gt6\) (1.6 ms) and \(gt9\) (0.4 ms) field gradients of strength 0.28 T/m. The other pulse gradients were of following strength and duration: \(g1 = 0.30\ \text{T/m and 1.0 ms}, \) \(g2 = 0.17\ \text{T/m and 0.75 ms}, \) \(g3 = 0.32\ \text{T/m and 1.0 ms}, \) \(g4 = 0.21\ \text{T/m and 0.30 ms}, \) \(g5 = 0.17\ \text{T/m and 0.20 ms}, \) \(g7 = 0.17\ \text{T/m and 1.0 ms},\) \(g8 = 0.28\ \text{T/m and 0.80 ms}.\) Quadrature detection in the \(t_1\) (\(^{13}\text{C}_X\) chemical shift) dimension was achieved by alternating the phase
of $\phi_1$ in a States-TPPI manner. Echo/anti-echo selection in the $t_2$ ($^{13}$C chemical shift) dimension was achieved by inverting the amplitude of the g6 gradient pulse and the phase $\phi_4$. The total experimental time was 21 h. The data were processed using Varian’s VNMR software using f1coef = ‘1, 0, 0, 0, 0,-1, 0’ and f2coef = ‘1, 0, -1, 0, 0, -1, 0, -1’. The raw data were linear predicted two times the number points sampled in the $t_1$ and $t_2$ dimensions, zero-filled to give a $512 \times 512 \times 4096$ matrix and then weighted with sinebell and shifted sinebell functions before Fourier transformation.

The pulse sequence for 3D gHC$_A$C$_X$ is shown in Figure 2.5.

![Pulse sequence for the HC$_A$C$_X$ experiment. Narrow (black) and wide (white) bars indicate 90° and 180° pulses, respectively.](image)

Figure 2.5. Pulse sequence for the HC$_A$C$_X$ experiment. Narrow (black) and wide (white) bars indicate 90° and 180° pulses, respectively.

2.3.3.2 Acquisition of 3D gHC$_A$C$_X$-HH-TOCSY NMR Spectra

The 3D gHC$_A$C$_X$-HH-TOCSY NMR spectrum was collected using the same parameters described above for gHC$_A$C$_X$ NMR. The TOCSY isotropic mixing time was 40 ms and was achieved using DIPSI-2 mixing sequence of strength $\gamma B_h = 7$ kHz. The data were linear predicted two times the number points sampled in $t_1$ and $t_2$ dimensions, zero-filled to give a $512 \times 512 \times 4096$ matrix and then weighted with sinebell and shifted sinebell functions before Fourier transformation.

The pulse sequence for 3D gHC$_A$C$_X$-HH-TOCSY is shown in Figure 2.6.
Figure 2.6. Pulse sequence for the HC$_A$C$_X$-HH-TOCSY experiment. Narrow (black) and wide (white) bars indicate 90° and 180° pulses, respectively.
CHAPTER III
CHARACTERIZATION OF THE POLYMERS BY MULTIDIMENSIONAL NMR

3.1 Introduction

The studies of ethylene-vinyl acetate or ethylene-carbon monoxide polymers have been of significant importance in the commercial field and hence have been studied extensively in the past using NMR. $^{13}$C NMR has been used in the past for the study of these polymers. Ibrahim et al.\textsuperscript{47} studied the tacticity effects polyV and monomer sequence distribution (MSD) in polyEV and found at least five MSD triad environments for five methylene groups and four MSD triad environments for four methine groups. Wu et al.\textsuperscript{31} used model compounds to assign resonances of polyEV. Randall\textsuperscript{17} studied polyEV at high temperature (120°C) to identify the resonances of triads and short alkyl chain branches. Although, these studies were extensive, the copolymers were examined at low field and using only 1D NMR methods.

From the study of 1D NMR it was observed that the spectra showed many overlapping patterns. This was observed especially in the methine regions of polyEV copolymer; the spectra can be more complicated in case of terpolymers. To solve this problem 2D NMR was used as it disperses the resonances in a second dimension and also helps to get atomic connectivity information and in the end confirm the resonances previously assigned. 2D COSY and HETCOR was use by Bruch and Payne\textsuperscript{18} for the
analysis of a variety of co- and terpolymers. They could assign resonances up to triad levels unambiguously and were also able to identify the end groups. Beshah\textsuperscript{19} utilized a more modern 2D technique to study polyEV. He used HSQC-TOCSY to obtain a combined proton-carbon and proton-proton correlations in a single experiment and was able to obtain much microstructural information of the polymer. Wyzgoski \textit{et al.}\textsuperscript{48} have used a variety of 2D NMR techniques for the analysis of a much more complicated polymer of ethylene, \(n\)-butyl acrylate and carbon monoxide. They performed the experiments at elevated temperatures to the increase the mobility and solve \(T_2\) relaxation problems and thus were able to determine various structures and chain ends present in the terpolymer. Due to the presence of \(n\)-butyl acrylate, which introduces a stereogenic center in the polymer, the structures in that region were overlapped and complex. To solve this problem and to disperse the resonances further, another dimension (3D NMR) was used.

Monwar \textit{et al.}\textsuperscript{29} studied a variety of \(^{13}\)C enriched polymers labeled at various positions of \(n\)-butyl acrylate and then used a suite of 3D NMR experiments, HC\_A\_C\_X and HC\_A\_C\_X-HH-TOCSY to completely assign the resonances of \(n\)-butyl acrylate centered n-ads up to pentad levels. A similar polymer is studied here of ethylene, vinyl acetate and carbon monoxide (polyEVC).

Initial studies of polyEVC were carried out using various 1D and 2D NMR methods. These studies were helpful to identify the resonance patterns up to triad levels. Various end groups and short chain branching structures were also identified. Some of the areas of the spectrum showed extreme overlap, especially the vinyl acetate resonances. To circumvent this problem and identify as many resonances as possible, 3D NMR experiments mentioned above were used. A \(^{13}\)C enriched polymer labeled at vinyl
acetate positions 1 and 2, with similar composition as the ones studied earlier was used for this purpose. All the polymer studies were carried out at high temperature (120 °C) and on a 750 MHz instrument. The NMR data on unlabeled and labeled polyEVC provided insight into the complex structural arrangement of these polymers.

3.2 Structures and Nomenclature

The nomenclature used to identify different atoms in the structures of polyEVC, is the same as that proposed by Wyzgoski et al.48 It is based on the one defined by Carmen49 and later modified by Dorman50 and Randall17 for polyethylene copolymers. For clarity it is described here. The general structure of polyethylene, 1, is shown at the top of Scheme 3.1. The carbons along the backbone of polyethylene containing short chain hydrocarbon branches are defined by a pair of Greek letters to indicate the distances, in both directions, from a branch point or a substitution. The carbons in a hydrocarbon chain branch are defined by $iB_n$, where ‘$i$’ designates the position in the branch, starting from the methyl group in position ‘1’, and ‘$n$’ gives the length of that branch. The saturated chain end carbons are designated as 1s, 2s, starting with carbon of the methyl group in position ‘1’. If the chain terminates by the formation of unsaturation the carbons involved in unsaturation are assigned as 1u, 2u starting with carbon of methylene group in position ‘1’, the successive saturated carbons are assigned as 1a, 2a etc.

The terpolymers contain structures resulting from the addition of E, V and C units in a variety of combinations. To define all the unique atoms in the structures the nomenclature proposed by Wyzgoski et al.48 is adapted here. In addition to the two Greek letters to indicate the distances, in both directions, to a branch point or a substitution, a
superscript ‘V’ or ‘C’ is used to indicate a branch formed from vinyl acetate or carbon monoxide units, respectively. If the in-chain methylene is longer than a certain number of bonds from the branch site it is indicated by superscripted ‘+’. The in-chain methine carbons are indicated by ‘CH’ with a subscript indicating the triad structure in which it is centered. For example, in a VEE triad, 2, the carbon next to the methine carbon with an acetate branch is designated as $\alpha^V$; the successive carbons are designated $\beta^V$ and $\gamma^V$. The continuation of the methylene carbon chain in the opposite direction is designated by the second Greek letter, $\delta^+$ indicating that the branch to the right along polymer backbone is in the $\delta$ position or further along the polymer chain. Similarly, in a CEV triad (7), the carbon adjacent to carbonyl group is designated as $\alpha^C\gamma^V$ since it is $\alpha$ to the C=O branch and it is the third carbon from the methine carbon branch point of a vinyl acetate unit. The next carbon to the right is two bonds away from branches in both the directions along the backbone; it is the second carbon from the carbonyl carbon of a C unit and the second carbon from the methine carbon of a V unit; hence it is designated by $\beta^V\beta^C$. The same system was applied to label groups in all the other triads relevant to the discussion.
The polymer might also contain short chain branching structures which are formed by intramolecular H-abstraction and rearrangements that occur during the polymerization process. McCord et al.\textsuperscript{23} have extensively studied the formation of short-chain branching in ethylene homopolymer and a variety of ethylene copolymers. Short chain branches are formed by ‘backbiting’ reactions in which the growing radical curls back to form an intermediate six or seven membered ring, transferring the chain end
radical back to the main chain by abstracting a hydrogen atom (intramolecular chain transfer). The mechanisms and the nomenclature used by McCord et al.\textsuperscript{23} to define the possible short chains branches have been used to describe the short-chains in this study. A general scheme for the possible short chain branch-formation reactions is shown in scheme 3.2.

**Scheme 3.2.** Possible short-chain branch formation mechanisms involving polymerization of ethylene with n-butyl acrylate monomer: a) H-abstraction by a comonomer radical-\(A_1B_4\) branch; b) H-abstraction across a comonomer radical- \(A_3B_4\); c) H-abstraction from a comonomer- \(A_QB_4\) butyl branch; d) double-backbiting mechanism involving H-abstraction from a comonomer unit- \(A_QB_2-B_2\).

Table 3.1 shows the different permutations of triad structures possible in polyEVC. The likelihood of C adding to a growing polymer chain containing terminal C
units is low; therefore, structures containing CC dyads are unlikely. At the field strengths used for contemporary NMR studies, the resonances are sensitive to pentad (and even heptad) structures. There can be as many as nine permutations of pentad monomer sequences for each triad structure in Table 3.1; so that potentially the polymer is a mixture of over 100 structure fragments.

Table 3.1. Possible triad sequences for polyEVC.

<table>
<thead>
<tr>
<th>E-centered</th>
<th>V-centered</th>
<th>C-centered</th>
</tr>
</thead>
<tbody>
<tr>
<td>EEE</td>
<td>EVE</td>
<td>ECE</td>
</tr>
<tr>
<td>EEV</td>
<td>EVC</td>
<td>ECC</td>
</tr>
<tr>
<td>EEC</td>
<td>EVV(2)</td>
<td>VCE</td>
</tr>
<tr>
<td>VEE</td>
<td>CVV(2)</td>
<td>ECV</td>
</tr>
<tr>
<td>VEV(2)</td>
<td>CVE</td>
<td>CCV</td>
</tr>
<tr>
<td>CEC</td>
<td>VVE(2)</td>
<td>VCV</td>
</tr>
<tr>
<td>VEC</td>
<td>VVV(4)</td>
<td>VCC</td>
</tr>
<tr>
<td>CEV</td>
<td>VVC(2)</td>
<td>CCE</td>
</tr>
<tr>
<td>CVC</td>
<td>CVC</td>
<td>CCC</td>
</tr>
</tbody>
</table>

aE=ethylene, V=vinyl acetate and C=carbon monoxide. The number in the parentheses indicate the number of triads stereosequences when more than one is possible.

3.3 Characterization of Unlabeled Poly(ethylene-co-vinyl acetate-co-carbon monoxide)

Four samples of polyEVC terpolymers with varying monomer compositions were analyzed by 1D ($^1$H, $^{13}$C) and 2D (HSQC, HMBC and HSQC-TOCSY) NMR methods at high temperature (120°C) on 750MHz NMR instrument. An effort to identify all the possible triad sequences from each monomer was made using the data from these experiments.
3.3.1 1D NMR Analysis and Quantitative Study

Figure 3.1 shows 1D $^1$H NMR spectra of polyEVC samples A (Figure 3.1a), B (Figure 3.1b), C (Figure 3.1c), and D (Figure 3.1d). All the spectra show similar peaks with characteristic intensity changes due to different compositions of E, V and C in the polymers. Sample A has a moderate amount of V and C units; hence it is used as a standard to compare all the other spectra.

![NMR Spectra Diagram]

Figure 3.1. 750 MHz $^1$H NMR spectra of polyEVC samples having varied monomer compositions: a) sample A (E=72%, V=13%, C=15%) , b) sample B (E=81%, V=9%, C=10%), c) sample C (E=68%, V=7%, C=25%), and d) sample D (E=70%, V=25%, C=5%).
All the samples show peaks at 0.87 ppm and at 1.96 ppm, which can be assigned to the methyl and –OCOCH$_3$ protons, respectively. The intensity of –OCOCH$_3$ proton resonance is highest in the sample D with highest content of V. The sample with highest C content shows an additional peak at 1.00 ppm; this could be assigned to a methyl group from CEc.e. Sample B has highest amount of E and hence the proton resonances from the methylene units at $\delta$ position show highest intensity in the $^1$H spectrum of sample B. All the other resonances are similar to those in sample A. Sample C shows the strongest resonances near 2.29 ppm and 2.58 ppm compared to rest of the samples. These resonances could be assigned to methylene protons $\alpha$ to the ketone carbonyl units. The resonance at 1.55 ppm was assigned to methylene protons $\alpha$ to a methine unit carrying an acetate group. This resonance shows increased intensity in sample C with highest C content while the intensity is lowest in sample with highest V content (sample D). This suggests that maybe vinyl acetate adds to other vinyl acetate units when it is in high concentration in the monomer feed and forms –VV– structures. The effect can also be observed on the methine protons. Thus, the sample D shows two major proton resonances near 5 ppm; the upfield resonance could be assigned to methine proton from EVE triad units and the downfield resonances near 5.01 ppm to methine protons from EVV units.

The EVV resonances show a small shoulder near 5.09 ppm and this could be assigned to methine protons from VVV triad units. A small resonance at about 5.26 ppm is also observed in the methine region which can be seen prominently in sample B; this resonances is much downfield may be due to a ketone carbonyl unit near it and hence was assigned to CVE units.
The downfield region of the proton spectrum shows two more unusual resonances at 6.07 ppm and 6.71 ppm. These resonances are seen more prominently in sample C. These resonances are speculated to be from an α-β unsaturated ketone unit. The polymers containing vinyl acetate are known to undergo degradation reactions releasing a molecule of vinyl acetate. From the resonances it can be speculated that may be the presence of ketone carbonyl unit next to the methylene unit of vinyl acetate facilitates the reaction giving rise to these unusual structures.

Regions from the $^{13}$C NMR spectra (peak-free regions omitted) of the four samples of polyEVC, A, B, C and D, are shown in Figure 3.2. The spectra show characteristic features due to their different compositions. As all the different possible peaks are observed in sample A, due to the moderate proportions of all the monomers, it was used as a benchmark to compare the peak intensities in the spectra from the rest of the samples studied. The spectrum of Sample B, with highest content of ethylene, shows the most intense peak at 30.00 ppm due to $\delta^+\delta^+$ carbons. Sample C, with highest carbon monoxide content shows an increase in the intensities of the peaks near $\delta_C=42$ and 24 ppm due to the $\alpha^C$ and $\beta^C$ methylene carbons of CEE-triads. There is also an increase in the intensity of the $\alpha^C\beta^C$ peak near 36 ppm due to 1, 4-dione of CEC structures. The $^{13}$C spectrum of sample D, with highest content of V units and the lowest content of C units, shows an increase in the intensities of $\alpha^V$ and $\beta^V$ methylene resonances of VEE/EEV triads near 34 ppm and 25 ppm, while the peaks from C-centered triads are small compared to the corresponding peaks in the spectra of samples A and C. As the V content in the polymer increases, the $\alpha^V\alpha^V$ methylene carbon peaks due to the less probable triads such as VVV and VVX/XVV are clearly observed in the spectrum near 39 ppm.
The methine carbon region also shows many additional resonances from various monomer- and stereo-sequences of \( \text{–VVX–} \) and \( \text{–VVV–} \) centered pentads.

**Sample A**

\( E=72\%, \ V=13\%, \ C=15\% \)

**Sample B**

\( E=81\%, \ V=9\%, \ C=10\% \)

**Sample C**

\( E=68\%, \ V=7\%, \ C=26\% \)

**Sample D**

\( E=70\%, \ V=25\%, \ C=5\% \)

Figure 3.2. 188.6 MHz \(^{13}\text{C}\) NMR spectra of polyEVC samples having varied monomer compositions: a) sample A, b) sample B, c) sample C and d) sample D.
The influence of varying the V and C content is also clearly seen in an expansion of the carbonyl region from the $^{13}$C spectrum. Sample D shows an increase in the intensities of the resonances from ester carbonyl carbons ($\sim 169.7$ ppm) compared to the corresponding regions of the spectra from samples A and C. It can also be seen that the intensity of this peak is similar to that of the resonance near 20 ppm from the acetate methyl carbon. Due to the high content of carbon monoxide units in sample C the ketone carbonyl intensities are greatly increased.

Though the methylene and methine resonances are well separated from each other, the extensive overlap and complexity of the resonance patterns within each group of peaks makes it impossible to do much more than these general resonance assignments using the 1D $^{13}$C NMR data. For the complete resonance assignments, experiments like 2D gHSQC, HMBC and HSQC-TOCSY are useful. They not only give atomic connectivity information, but also disperse the spectrum into a second dimension so that overlapping resonances in the 1D spectrum can be resolved and assigned unambiguously.

Quantitative NMR Analysis of Poly(ethylene-co-vinyl acetate-co-carbon monoxide): Quantitative analysis using $^{13}$C NMR was done on all the four samples (A, B, C, and D) of poly(ethylene-co-vinyl acetate-co-carbon monoxide). The spectra were collected with gated decoupling and a relaxation delay of five times the longest $T_1$ (carbonyl carbons had the longest $T_1$s of 4-5 s) was used to circumvent any erroneous calculations due to the nuclear Overhauser effect (NOE). The areas were integrated and each carbon integration was compared per 1000 carbons.

Three major resonances are observed in the ketone carbonyl region. Resonances from 208.75 ppm to 207.91 ppm are assigned to XECEX pentads, resonances from
207.87 ppm to 207.08 ppm are assigned to XECEV pentads while resonances at 206.09 ppm to 205.35 ppm are assigned to XECVX pentads. The integrated areas observed for the total ketone carbonyl region was observed to be 60 for Sample A, 44 for Sample B, 124 for Sample C due to highest carbon monoxide content and 15 for Sample D due to lowest carbon monoxide content.

Ester carbonyl resonances are observed from 170.08 ppm to 169.10 ppm. Integration of this area for Sample D with highest vinyl acetate content (~ 55%) measures 112, while Sample A with ~28% of V measures 66, sample B with ~20% V measures 44 and sample C with ~41% measures 41.

Estimation of the number of ester carbonyl carbons per 1000 carbons can also be obtained for the study of integrated area of methyl resonances (21.07 ppm to 20.38 ppm) as the values for both the areas are observed to be very similar. This is observed as integration values could be obtained without the discrepancy of overlap from other peaks also the two carbons are least sensitive to structural and stereochemical changes in the backbone chain as the other carbons are.

Methylene resonances from n-ads obtained from XECEX pentads are observed at ~43.4ppm to ~41.7ppm due to $\alpha^C\delta^+$ and at ~24.7ppm to ~23.4ppm are due to $\beta^C\delta^+$. The integrated areas as expected are in 1:1 ratio for all the four samples. As expected the integration values ($\alpha^C\delta^+$, 157; $\beta^C\delta^+$, 152) of Sample C with highest carbon monoxide content are much higher than Sample A ($\alpha^C\delta^+$, 100; $\beta^C\delta^+$, 99), Sample B ($\alpha^C\delta^+$, 89; $\beta^C\delta^+$, 81) and Sample D ($\alpha^C\delta^+$, 29; $\beta^C\delta^+$, 29) but almost twice the integrated areas of ketone carbons.
Theoretically, a similar comparison could be obtained between $\alpha^V\delta^+$ and $\beta^V\delta^+$ so that the integrated areas are in 1:1 ratio. Study of the all the four samples show that the integrated areas of $\alpha^V\delta^+$ is actually much higher that that of $\beta^V\delta^+$. This incongruity is not unexpected as the contribution to the integrated area of resonances from $\sim35.5$ ppm to $\sim33.8$ ppm is not only due to $\alpha^V\delta^+$ but also from $\alpha^V\gamma^V/C$ and some other unresolved resonances, while the resonances from $\sim25.9$ ppm to $\sim24.9$ ppm are purely due to $\beta^V\delta^+$ carbons. Integrated areas of $\alpha^V\delta^+$ and $\beta^V\delta^+$ for the Sample D with highest vinyl acetate content were observed to be 139 and 93, respectively, Sample A shows the integrated area to be 83 and 60, respectively, Sample B shows the integrated area to be 78 and 53, respectively, and Sample C shows the integrated area to be 44 and 31, respectively.

To calculate the composition of the three monomers in all the terpolymers the spectrum was subdivided into five major sections; section $A$ (204.5-212.3 ppm), section $B$ (168.8-170.5 ppm), section $C$ (67.1-75.2 ppm), section $D$ (20.2-21.1 ppm) and section $X$ (7.7-48.1 ppm). Figure 3.3 shows the five sections of the $^{13}$C spectrum used for the quantitative analysis.

![Figure 3.3 Typical $^{13}$C NMR spectrum of polyEVC showing five major sections, $A$, $B$, $C$, $D$, and $X$, used in the quantitative analysis of the polymers.](image-url)
Region A represents the ketone carbonyl carbon region, hence can be used directly to calculate the amount of carbon monoxide. The number of moles of carbon monoxide can be calculated from the sum of integration values of the resonances from region \( A \). The amount of vinyl acetate can be calculated from three different areas, section \( B \) which is representative of ester carbonyl carbons, section \( C \) which is the methine carbon region of vinyl acetate and section \( D \) which is the methyl carbon region from the acetate group of vinyl acetate. The integrated areas of the three regions were found to be similar hence the three areas were averaged to calculate the number of moles vinyl acetate. The amount of ethylene in the polymer can be calculated from section \( X \). This area is representative of resonances from ethylene (two carbons of ethylene) and vinyl acetate (one carbon from methyl, methylene and methine, each) units. Thus, the number of moles of ethylene can be calculated by subtracting the moles of vinyl acetate from section \( X \). Table 3.2 summarizes the formulas and the results from the compositional analysis for all the four terpolymers using \(^{13}\text{C}\) NMR.

Table 3.2. Compositional analysis of Polymers A, B, C and D using \(^{13}\text{C}\) NMR.

<table>
<thead>
<tr>
<th>monomer</th>
<th>formulas</th>
<th>terpolymer composition(mole %)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>([X-2(B+C+D)/3]/2S)×100</td>
<td>(\begin{tabular}{l} A \ B \ C \ D \end{tabular})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\begin{tabular}{l} 72 \ 81 \ 67 \ 70 \end{tabular})</td>
</tr>
<tr>
<td>V</td>
<td>([(B+C+D)/3S])×100</td>
<td>(\begin{tabular}{l} A \ B \ C \ D \end{tabular})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\begin{tabular}{l} 13 \ 9 \ 7 \ 25 \end{tabular})</td>
</tr>
<tr>
<td>C</td>
<td>([A/S])×100</td>
<td>(\begin{tabular}{l} A \ B \ C \ D \end{tabular})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\begin{tabular}{l} 15 \ 10 \ 26 \ 5 \end{tabular})</td>
</tr>
</tbody>
</table>

* \( A \) = total integral value for region \( A \)
* \( B \) = total integral value for region \( B \)
* \( C \) = total integral value for region \( C \)
* \( D \) = total integral value for region \( D \)
* \( X \) = total integral value for region \( X \)
* \( S \) = total number of moles of ethylene, vinyl acetate and carbon monoxide

\( S = A + (B+C+D)/3 + (X-2[(B+C+D)/3]) \)
Quantitative analysis of the four polymers of polyEVC was also conducted using $^1$H NMR. $^1$H NMR of the polymer shows three groups of resonances; the two resonances between 6.8 ppm to 5.8 ppm were assigned to an $\alpha$-$\beta$ unsaturated ketone, groups of resonances from 5.3 ppm to 4.6 ppm were assigned to various methine protons, while the groups of resonances from 3.1 ppm to 0.6 ppm were assigned to various methylene and methyl protons. The resonances in these three areas were integrated and each proton integration value was compared to per 100 protons.

To calculate the amount of vinyl acetate in the polymer the integrated areas from methine resonances and the two resonances from $\alpha$-$\beta$ unsaturated ketone were used as these areas purely represent the vinyl acetate present in the polymer sample. The sample with highest amount of carbon monoxide shows proton resonances due to $\alpha$-$\beta$ unsaturations very prominently. This is due to the fact that as the carbon monoxide amount increases in the sample the probability of obtaining C next to a V unit increases and hence the integrated area was observed to be highest (sample A: 0.12, sample B: 0.05, sample C: 0.37, sample D: 0.12). As sample D has highest amount of vinyl acetate this sample shows the highest integrated area for the methine region (sample A: 3.13, sample B: 2.24, sample C: 1.63, sample D: 6.08).

The carbon monoxide amount in the polymer sample was calculated using two $\alpha^C$ methylene resonances, 3.1 ppm to 2.49 ppm ($\alpha^C\beta^C$) and 2.49 ppm to 2.12 ppm ($\alpha^C\delta^+/\alpha^C\gamma$). As the carbon monoxide amount increases in the sample not only the $\alpha^C\delta^+/\alpha^C\gamma$ resonance increases in intensity but the $\alpha^C\beta^C$ resonance also becomes a prominent resonance in the spectrum and hence in the calculation of the C content in the polymer both the resonances are taken into consideration. The integrated areas for all the
four polymer in $\alpha^C\delta^+$/\(\alpha^C\gamma\) and $\alpha^C\beta^C$ is as follows: sample A: 12.91, 2.28; sample B: 9.94, 1.38; sample C: **22.55, 13.72**; sample D: 4.31, 0.26. Table 3.3 summarizes the results and the formulas used to calculate the mole fraction of E, V and C in all the four polymers.

Table 3.3 Compositional analysis of Polymers A, B, C and D using $^1$H NMR.

<table>
<thead>
<tr>
<th>monomer</th>
<th>formulas</th>
<th>terpolymer composition (mole %)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>$[(X-6V)/4S]\times100$</td>
<td>A: 74 B: 81 C: 67 D: 68</td>
</tr>
<tr>
<td>V</td>
<td>$[V/S]\times100$</td>
<td>12 9 5 27</td>
</tr>
<tr>
<td>C</td>
<td>$[C/4S]\times100$</td>
<td>14 11 27 5</td>
</tr>
</tbody>
</table>

**E** = ethylene  
**V** = vinyl acetate  
**C** = carbon monoxide  
$X$ = total integral region = $4E+6V+Us$  
$U$ = $\alpha-\beta$ unsaturated ketone region  
$S$ = total number of moles = $(X+C-2V)/4$

3.3.2 2D NMR Study

The HSQC spectrum exhibits correlations between the resonances of $^1$H and $^{13}$C atoms having one-bond couplings ($^1$J$_{CH}$), providing information about connectivity between directly bound $^1$H and $^{13}$C atoms. These correlations are labeled a, b, c, etc. in the spectra. The HSQC spectrum helps to separate the methylenes from the methyl and methine correlations by virtue of the relative signs of the cross-peaks, in place of the 1D DEPT experiment normally used for this purpose.

Figures 3.4a and 3.4b show the methyl/methylene and methine regions, respectively, from HSQC spectra of sample A. From the spectra it can be observed that the methyl, methylene and methine resonances are well separated from each other thus
avoiding any phase distortions or cancellation due to the overlap of positive methine and methyl, and inverted methylene cross-peaks. The peaks in the HSQC spectrum can be related to multiple-bond correlations in two HMBC spectra obtained using delays optimized for 10 Hz and 5 Hz couplings, respectively (multiple bond delay set to \( \tau_{mb} = 1/2^n J_{CH} = 0.05 \) and 0.10). This was done to optimize detection of cross-peaks from two- and three-bonds \(^1H\)-\(^{13}C\) couplings. These multiple-bond correlations are labeled \( a_n, b_n, c_n \) etc. where the letters designates a specific \(^{13}C\) chemical shift corresponding to the HSQC cross-peak, and the numerical subscript \( n \) is used to number each of the multiple HMBC correlations at this \(^{13}C\) chemical shift. For example, cross peak \( a \) in the HSQC spectrum can be related to several HMBC cross-peaks; \( a_1, a_2, a_3, \) etc., at the same \(^{13}C\) chemical shift. To confirm the connectivity, a 2D-HSQC-TOCSY experiment was also employed. It gives connectivity between the resonances of \(^{13}C\) atoms and the resonances of all the protons which are part of the spin system of the \(^1H\) atom bound to it. The experiment becomes a very useful tool as it provides the heteronuclear and homonuclear correlations in a single 2D experiment, and sometimes reveals correlations not observed in the HMBC spectrum due to cancellations from overlapping antiphase multiplet components\(^{36}\). In HSQC-TOCSY spectrum, both one-bond and multiple-bond C-H correlations are found. These are designated with the same labels as those used for the corresponding cross-peaks in the HSQC and HMBC spectra. The most intense cross-peak observed in the HSQC spectrum near \( \delta_C=30 \) ppm and \( \delta_H=1.29 \) ppm, is due to the \( \gamma \delta^+ \) and \( \delta^- \delta^+ \) protons and carbons from various triads. Resonance assignments from the various experiments employed are summarized in Table 3.3.

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Figure 3.4. Selected regions from the 2D HSQC NMR spectra showing, a) methyl and methylene, b) methine carbon region of sample A.
### Table 3.4. NMR resonance assignments of polyEVC.

<table>
<thead>
<tr>
<th>Region</th>
<th>Assignment</th>
<th>Previous works*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1S</td>
<td>CE</td>
</tr>
<tr>
<td></td>
<td>1A-B1</td>
<td>A-B4</td>
</tr>
<tr>
<td></td>
<td>B4</td>
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</tr>
<tr>
<td></td>
<td>1B</td>
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<tr>
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<td>1B</td>
<td>CEE</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>β'β''</td>
<td>CEV</td>
</tr>
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Digital resolution: \( \gamma_1 = 1.1 \text{ Hz/pt}; \gamma_2 = 0.6 \text{ Hz/pt} \)
**E-centered Triads:** The group of cross peaks in HSQC (Figure 3.4a and Figure 3.5) at $\delta_C=25.5$ ppm and $\delta_H=1.33$ ppm are from $\beta^V\delta^+$ methylene correlations in VEE/EEV triads and show fine structure due to the effect of neighboring monomer units (E or V or C). The VEEE tetrads shows cross peaks in HSQC slice (cross-peak h') at $\delta_C=25.65$ ppm and $\delta_H=1.33$ ppm due to $\beta^V\delta^-$ and show HMBC correlations to the non-equivalent $\alpha^V\delta^+$ protons at $\delta_H=1.30$, 1.56 ppm (cross-peak h'$_1$) and to $\text{CH}_{\text{EVE}}$ at $\delta_H=4.94$ ppm (cross-peak h'$_4$). The cross-peak at $\delta_C=25.47$ ppm and $\delta_H=1.33$ ppm (cross-peak h'') in the HSQC slice is due to the VEEC tetrad as it show correlations to the two neighboring protons at $\delta_H=1.54$, 1.29 ppm (due to $\alpha^V\delta^C$, cross-peak h''$_1$) and at $\delta_H=1.58$ ppm (due to $\beta^C\gamma^V$, cross-peak h''$_2$). It shows additional correlations to $\alpha^C\delta^V$ protons at $\delta_H=2.29$ ppm (cross-peak h''$_3$) and one down field signal at $\delta_H=4.94$ ppm (cross-peak h''$_4$) due to methine proton. Another HSQC correlation (cross peak h''') can be observed next to cross peak h'' which shows similar correlations to h'' in the HMBC spectrum. This could be due to the effect of another group on the other side of V but the assignment of it could not be done due to the lack of any further information in the HMBC spectrum. Thus the cross peak h''' was assigned to XVEEC structure.
Figure 3.5. Selected regions from the 2D HSQC (top) and HMBC (bottom) NMR spectra of sample A showing $\beta^V\delta^+$ cross peaks of VEE/EEV triads.

The group of resonances at $\delta_C \approx 24$ ppm and $\delta_H \approx -1.60$ ppm in Figure 3.4a is due to the $\beta^C\delta^+$ methylene protons and carbons from CEE triads. Figure 3.6 shows HSQC correlations to the $\beta^C$ methylene carbon resonances in the CEE triad. Cross peaks at
\[ \delta_C = 24.31 \text{ ppm and } \delta_H = 1.57 \text{ ppm (cross peak } g') \text{ due to } \beta^C\delta^+ \text{ of ECEE tetrad in HSQC show correlations to the protons of } \alpha^C\delta^+ \text{ at } \delta_H = 2.29 \text{ ppm (cross peak } g'_3) \text{ and protons of } \gamma^C\delta^+ \text{ at } \delta_H = 1.28 \text{ ppm (cross peak } g'_1) \text{ in the HMBC spectra. The cross peaks } g'' \text{ (}\delta_C = 23.94 \text{ ppm and } \delta_H = 1.55 \text{ ppm)} \text{ in the HSQC spectrum is due to the effect of another } C \text{ unit in the } \gamma \text{ position to give } \beta^C\gamma^C \text{ methylene carbon in ECEEC pentad. It shows correlation to the other } \beta^C\gamma^C \text{ methylene proton resonances at } \delta_H = 1.55 \text{ ppm (cross peak } g''_2). \text{ Correlation to } \alpha^C\delta^C \text{ proton resonance is observed at } \delta_H = 2.29 \text{ ppm (cross peak } g''_3) \text{ in the HMBC spectrum. The cross peak } g'' \text{ (}\delta_C = 24.10 \text{ ppm and } \delta_H = 1.56 \text{ ppm)} \text{ in the HSQC spectrum is also due to the } \beta^C \text{ methylene group and shows correlations at the same positions in the HMBC as that seen for } g'' \text{. This cross peak could be due to CEEX or XCEE structures. As } C \text{ does not add to another } C \text{ unit hence a } V \text{ unit could present next to } C \text{ and as the unit it too far away (4 bonds) to be detected in the HMBC spectrum it could not be assigned unambiguously in the polymer.} \]
Figure 3.6. Selected regions from the 2D HSQC (top) and HMBC (bottom) NMR spectra of sample A showing $\beta^C_{\delta^+}$ cross peaks of CEE triads.

Figure 3.7 shows the region from the HSQC spectrum of sample A; containing the $\beta^V_{\beta^V}$ and $\beta^V_{\beta^C}$ cross-peaks from VEV and CEV triads, respectively, and the corresponding region from the HMBC spectrum showing the multiple-bond correlations.
to resonances of neighboring $^1$H atoms. The $\beta^V\beta^V$ (cross-peaks f) from VEV triads is observed at $\delta_C=21.42$ ppm and $\delta_H=1.39$ ppm. This carbon resonance shows a two bond correlation to the $\alpha^V\gamma^V$ proton resonance at $\delta_H=1.59$ ppm (cross-peak f$_1$) and a long range correlation to a methine proton at $\delta_H=4.90$ ppm (cross-peak f$_2$). Another weak resonance (cross peak f', $\delta_C=21.53$ ppm and $\delta_H=1.41$ ppm) was observed in the HSQC spectrum which also shows correlations at f'$_1$ ($\delta_H=1.56$ ppm) and to a methine proton at f'$_2$ ($\delta_H=4.89$ ppm) in the HMBC spectrum. This resonance could be due to higher n-ads of VEV but as no sufficient evidence of the neighboring groups was available it was assigned to XVEV tetrad. The presence of a carbonyl carbon in $\gamma$-position of a CEV triad instead of an acetate group in a VEV triad shifts the methylene carbon resonance upfield while the protons are shifted downfield. The $\beta^C\beta^V$ resonance of CEV triads is thus observed at $\delta_C=20.01$ ppm and $\delta_H=1.62$ ppm (cross-peak d). It shows correlation to two methylene protons two bonds away at $\delta_H=1.55$ ppm (cross-peak d$_1$) and $\delta_H=2.32$ ppm (cross-peak d$_2$) due to the $\alpha^V\gamma^C$ and $\alpha^C\gamma^V$ groups, respectively and a three bond correlation to the CH$_{\text{CEVEX}}$ methine proton at $\delta_H=4.91$ ppm (cross peak d$_3$).
Figure 3.7. Selected regions from the 2D HSQC (top) and HMBC (bottom) NMR spectra of sample A showing $\beta^V\beta^V$ and $\beta^C\beta^V$ cross peaks of VEV and CEV triads.

The addition of vinyl acetate in an opposite manner may take place during the polymerization process; this can be observed in the CE $\overline{V}$ triads (indistinguishable from VEC triads). Figure 3.8 shows the regions from HSQC-TOCSY spectrum containing VEC triad cross-peaks. The HSQC-TOCSY spectrum shows correlations to protons in a coupled spin system in addition to one-bond carbon-proton correlation. The $\alpha^V\beta^C$ resonance (cross-peak i) due to the one-bond carbon-proton correlation is observed at
$\delta_{C}=28.80$ ppm and $\delta_{H}=1.79, 1.90$ ppm. Correlations to $\alpha^C\beta^V$ (cross-peak $i_1$) and $\text{CH}_{\text{XEVEC}}$ (cross-peak $i_2$) proton resonances are observed at $\delta_{H}=2.37$ ppm and $\delta_{H}=4.91$ ppm, respectively. Similarly a one-bond carbon-proton correlation to the $\alpha^C\beta^V$ proton resonance (cross-peak $m$) is obtained at $\delta_{C}=38.72$ ppm and $\delta_{H}=2.37$ ppm while a clear correlation to the non-equivalent $\alpha^V\beta^C$ protons (cross-peaks $m_1$) is seen at $\delta_{H}=1.79, 1.90$ ppm; correlation to the $\text{CH}_{\text{XEVEC}}$ proton (cross-peak $m_2$) is seen at $\delta_{H}=4.91$ ppm.

Figure 3.8. Selected regions from the 2D HSQC-TOCSY NMR spectra of sample A showing $\alpha^V\beta^C$ and $\alpha^C\beta^V$ cross peaks of VEC triads.
The CEC triad is a very symmetrical triad and has one type of carbon between two ketone carbonyl carbons, the $\alpha^C\beta^C$ carbon. The $\alpha^C\beta^C$ one-bond C-H correlation is observed at $\delta_C=36.37$ ppm and $\delta_H=2.57$ ppm in HSQC shows correlation in HMBC at the same chemical shift ($\delta_H=2.57$ ppm) as in HSQC as both the $\alpha^C\beta^C$ carbons and protons are equivalent.

The group of resonances observed in the downfield region at $\delta_C=\sim42.5$ ppm and $\delta_H=2.29$ ppm of the HSQC spectrum (Figure 3.4a) is due to $\alpha^C$ carbons and protons of CEE triads. Two of tetrads ECEE (cross peak $p'$) and ECEV (cross peak $p^{4'}$) could be identified from that group and are shown in Figure 3.9. The $\alpha^C\delta^+$ resonances of ECEE tetrad is observed at $\delta_C=42.85$ ppm and $\delta_H=2.29$ ppm while the $\alpha^C\gamma^V$ carbon resonance from the ECEV tetrad is shifted upfield to $\delta_C=42.38$ ppm due to the $\gamma$-gauche effect; the proton resonance is observed at $\delta_H=2.32$ ppm. The $\alpha^C\delta^+$ resonance of ECEE tetrads show correlations to the $\gamma^C\delta^+$ protons at $\delta_H=1.28$ ppm (cross peak $p'_1$) and to $\beta^C\delta^+$ protons at $\delta_H=1.57$ ppm (cross peak $p'_2$). The ECEV tetrad shows correlations to $\beta^C\beta^V$ protons at $\delta_H=1.62$ ppm (cross peak $p^{h_2}$), to $\alpha^V\gamma^C$ protons at $\delta_H=1.57$ ppm (cross peak $p^{h_1}$) and a weak correlation to the methine proton at $\delta_H=4.90$ ppm (cross peak $p^{h_3}$). Two more cross peaks ($p^{2'}$ and $p^{3'}$) were also observed in the HSQC-TOCSY spectrum which could not be identified due to lack of additional information. As they showed correlations similar to ECEE tetrad they were assigned to ECEEX/XECEE pentad structures.
Figure 3.9. Selected regions from the 2D HSQC-TOCSY NMR spectra of sample A showing $\alpha^C$ cross peaks of CEE and CEV triads.

All the $\alpha^V\delta^+$ and $\alpha^V\gamma^C$ resonances are observed near $\delta_c=34.4$ ppm and $\delta_H=1.60$ ppm in the plot of the regions from the HSQC-TOCSY spectrum shown in the Figure 3.10. The HSQC peak pattern is extremely complex due to the various $\alpha^V\gamma^X$ resonances in this region. The substitution at the $\gamma$ position has a very minor effect on the chemical shift of the $\alpha^V\gamma^X$ carbons hence the correlations show severe overlap. The most upfield correlation ($\delta_c=34.20$ ppm and $\delta_H=1.56$ ppm, cross-peak k') is due to the $\alpha^V\gamma^C$ methylene groups of CEVE tetrads. This carbon shows correlations to the resonances of three types.
of neighboring protons: correlation $k'_1$ to the $\beta^V\beta^C$ proton resonance, correlation $k'_2$ to the $\alpha^C\gamma^V$ proton resonance and correlation $k'_3$ to the CH$_{CEVE}$ proton resonance. The $\alpha^V\delta^+$ signal (cross-peak $k''$) due to EEVE tetrads is observed at $\delta_C=34.65$ ppm and $\delta_H=1.57$ ppm in HSQC-TOCSY spectrum and the $\alpha^V\delta^+$ carbon resonance shows correlations to the resonances of neighboring $\beta^V\delta^+$ protons (cross-peak $k''_1$) and to the methine proton at $\delta_H=4.94$ ppm (cross-peak $k''_2$). The most downfield correlation ($k'''$), is observed at $\delta_C=35.20$ ppm and $\delta_H=1.55, 1.60$ ppm, is at the $^{13}$C shift of the resonance from the $\alpha^V\delta^+$ methylenes of VVEX tetrads. This carbon resonance shows correlations to the $\beta^V\delta^+$ proton resonance (cross-peak $k'''_1$) at $\delta_H=1.34$ ppm and to the CH$_{XVVE}$ methine proton resonance at $\delta_H=5.05$ ppm (cross-peak $k'''_2$).
Figure 3.10. Selected regions from the 2D HSQC-TOCSY NMR spectra of sample A showing $\alpha^\gamma\delta^+$ and $\alpha^\gamma\gamma^C$ cross peaks.

**V-centered Triads:** Although $\alpha^\gamma\alpha^\gamma$ methylene carbon resonances from XVVE and XVVV tetrads are very close in $^{13}$C 1D spectrum, 2D experiments help to disperse them into two distinct sets of contour-peak patterns as seen in the HSQC-TOSCY
spectrum in Figure 3.11, which provides information about the neighboring groups in XVVE and XVVV tetrads.

The cross peaks n in HSQC-TOCSY spectrum are due to one-bond correlations between $\alpha^V\alpha^V$ methylene group carbon and proton resonances of EVVE tetrads ($\delta_C=39.34$ ppm and two non equivalent proton at $\delta_H = 1.78, 1.91$ ppm). Correlations are observed to the neighboring methine proton at $\delta_H = 5.03$ ppm (cross peak n$_2$) and to the $\alpha^V\delta^+$ protons at $\delta_H=1.61$ ppm (cross peak n$_1$). A symmetric structure would result in a correlation to one CH proton resonance as observed in the case of EVVE tetrad. While the $\alpha^V\alpha^V$ methylene in the central VV dyad in a EVVV tetrad shows two resolved one-bond C-H correlation in the HSQC-TOCSY spectrum which was not evident in HMBC. These cross peaks are due to proton resonances of CH$_{EVV}$ and CH$_{VVV}$ groups on either side (cross peaks o$_1$ and o$_2$) respectively.
Addition of carbon monoxide to vinyl acetate is expected to occur preferentially with carbon monoxide adding to the methylene carbon of vinyl acetate, $E \overline{V} C\cdot$. This is due to the high hindrance given by the acetate pendant group to addition of C=O. This same structure is produced when V follows C, $ECV\cdot$. The resonance observed at $\sim 47$ ppm in $^{13}$C 1D spectrum of all four polymers is consistent with the shift of $\alpha^C \alpha^V$ carbons in CV dyads. The intensity of this peak is highest in Sample C. Due to the effect of the ketone carbonyl and the methine carbon with an acetate group in the $\alpha$ position, the $\alpha^C \alpha^V$ resonance from the CVE triad is observed in the downfield region ($m\delta_c=47.38$ ppm, $m\delta_h$...
The two diastereotopic protons show TOCSY correlations to only the neighboring methine proton at $\delta_H=5.28$ ppm.

Various CH$_{XVX}$ methine correlations are observed between $\delta_C=70$-$75$ ppm and $\delta_H=4.80$-$5.30$ ppm (Figure 3.4b). The cross peaks due to the XE$\backslash$EX, VE$\backslash$XX, XX$\backslash$EV, CE$\backslash$XX, XX$\backslash$EC pentads are observed between $\delta_C=73$-$75$ ppm and $\delta_H=4.85$-$4.95$ ppm. The region to the right of this ($\delta_C=70$-$72$ ppm) contains correlations from CH$_{VVE/EEV}$. 
Group of resonances observed between $\delta_C=70.54-71.01$ ppm but much further downfield than all the other resonances in $f_2$ dimension are due to the CVE triads or $\overline{V}$ CE.

The HSQC-TOCSY gave better connectivity information here; hence it was used to assign the major methine resonances (Figure 3.13). This is often observed to be the case in sterically crowded regions. The most downfield resonance (cross peak $t'$, $\delta_C=74.46$ ppm and $\delta_H=4.93$ ppm) is due to CH$_{EEVE}$ and shows correlations to $\alpha^V\delta^+$ protons at $\delta_H=1.56$ ppm ($t'_2$) and to $\beta^V\delta^+$ protons at $\delta_H=1.33$ ppm ($t'_1$). The CH$_{VEVE}$ resonance is observed at $\delta_C=74.15$ ppm and $\delta_H=4.91$ ppm (cross peak $t''$). Wu and Ovenall$^{31}$ had observed methine resonance of EEVE pentad in polyEV at 74.1 ppm. The next upfield resonance is assigned to CH$_{XXVE}$, which is observed at $\delta_C=74.00$ ppm and $\delta_H=4.91$ ppm (cross peak $t'''$) and shows correlations to $\alpha^V\beta^C$ protons at $\delta_H=1.80, 1.93$ ppm ($t'''_3$) and to the $\alpha^C\beta^V$ protons at $\delta_H=2.38$ ppm ($t'''_4$). Further correlations at $\delta_H=1.56$ ppm and at $\delta_H=1.33$ ppm (due to $\alpha^V\delta^+$, $t''''_2$ and $\beta^V\delta^+$ protons, $t''''_1$) confirms the presence of an ethylene unit on the other side of ‘V’ in XXVE pentad.

The methine resonances of VVE triads (Figure 3.13) occur in two groups, the first group containing cross peaks from racemic ($r$) VV dyads (cross peak $r'$, $\delta_C=70.84$ ppm, $\delta_H=5.04$ ppm) and a second group containing cross peaks from meso ($m$) VV dyads (cross peak $s$, $\delta_C=71.64$ ppm, $\delta_H=5.01$ ppm) due to relative orientations of the acetate branches. At the $^{13}$C shift of the $m$-CH$_{VVE}$ in the HSQC-TOCSY cross peaks are seen to the $\alpha^V\delta^+$ protons at $\delta_H=1.60$ ppm (cross peak $s_1$) and to the non-equivalent $\alpha^V\alpha^V$ protons at $\delta_H=1.79$ and 1.93 ppm (cross peak $s_2$). Racemic methine carbon resonance are
correlated to $\alpha^V\delta^+$ protons at $\delta_H=1.60$ ppm (cross peak $r'_1$) and to only a single proton resonance from equivalent $\alpha^V\alpha^V$ protons at $\delta_H=1.80$ ppm (cross peak $r'_2$).

In CVE triads, due to the presence of the ketone carbonyl group in the $\beta$ position relative to the CH$_{CVE}$, the methine proton resonance is downfield (Figure 3.4b) compared to the CH$_{EVE}$ and CH$_{VVE}$. The approximate probability ratio of EVV to CVE is equal in this polymer based on the composition. Cross peaks from these triads are observed in the HSQC spectrum (Figure 3.14) at $\delta_C=70.96$ ppm and $\delta_H=5.27$ ppm (cross peak $r''$); correlations to the diastereotopic $\alpha^C\alpha^V$ protons are observed at $\delta_H=2.53$ and 2.67 ppm (cross peaks $r''_1$) in the HMBC spectrum.
Figure 3.13. Selected regions from the 2D HSQC-TOCSY NMR spectra of sample A showing methine resonances of EVE, VEC, VEV, m- and r-VVE triads.
Study of the $^{13}$C spectrum of Sample D (Figure 3.2d) in the methine region ($\delta_C = 67.4 - 69.4$ ppm) shows additional peaks compared to those found in the spectra from the other three samples. These are attributed to the VVV triads which are much more probable in this polymer having high V-content. The relevant HSQC spectrum of the methine region is shown in Figure 3.15. The region shows that the peaks are widely separated into two groups along the proton chemical shift dimension. By analogy with the results for EVV and CVE triads, the peaks near $\delta_C = 68$ ppm ($\delta_H = 5.1$ ppm) can be assigned to VVV triads and the resonances $\delta_C = 67.59$ ppm and $\delta_C = 68.31$ ppm with the
proton chemical shift $\delta_H=5.31$ ppm and $\delta_H=5.34$ ppm to CVV triads. Two peaks are observed most likely due to the stereochemical arrangements (m and r) of the acetate pendant groups.

![Figure 3.15. Selected region from the 2D HSQC NMR spectrum of sample D showing XVVVX and XCVVX methine resonances.](image)

**Ester Carbonyl Resonances:** The ester carbonyl carbons are away from the main chain and hence are not as sensitive to the changes in the monomer structure two or three units down the chain. Nevertheless, they showed some sensitivity towards the monomer sequence effects in triads. The HMBC slices in Figure 3.16 show correlations between the ester-carbonyl carbon and methyl protons. Very minor correlations can also be observed to the methine protons. Figure 3.16 shows the correlations of ester carbonyl carbons in various triads to the methyl protons and the corresponding methine protons. The three easily identified ester carbonyl carbon resonances are from XEV\textsubscript{EX}, XEV\textsubscript{VE} and XCV\textsubscript{EX} pentads. All the XEV\textsubscript{EX} ester carbonyl carbon resonance at $\delta_C=169.70$ppm show correlations to the methyl protons at $\delta_H=1.96$ppm (cross peak u'\textsubscript{1}) and to the methine proton resonance at $\delta_H=4.91$ppm (cross peak u'\textsubscript{2}).

Replacement of an E unit in EVE triads with a V unit to produce EVV triads shifts the ester carbonyl carbon resonance upfield ($\delta_C=169.59$ppm). Correlations from this
carbon resonance are observed with the methyl protons at δ_H=2.03ppm (cross peak u''_1) and methine proton resonance at δ_H=5.00ppm (cross peak u''_2). Replacement of E unit in EVE triads with a C to produce CVE triads also shifts the ester carbonyl carbon resonance up field (δ_C=169.40ppm), but only slightly. Correlations from this carbon resonance are observed with the methyl protons at δ_H=1.93ppm (cross peak u'''_1) and to the methine proton at δ_H=5.27ppm (cross peak u''''_2).

Figure 3.16. Selected regions from the 2D HMBC NMR spectra of sample A showing ester carbonyl resonances.

**C-Centered Triads:** The ketone carbonyl carbon resonances are observed in three groups, centered at 208 ppm (ECE), 207 ppm (VECX, CECXX) and at 206 ppm
(XECVX) (Figure 3.2 and Figure 3.17). Figure 3.17 shows all the ketone carbonyl resonances in the HMBC spectrum of sample A. The ketone carbonyl carbon at 208.68 ppm is due to the ECE triad and shows correlations to the α and β protons at 2.30 ppm (cross peak x₂) and 1.58 ppm (cross peak x₁), respectively. Addition of a V next to an E in ECE triad shifts the ketone carbonyl resonance upfield. Thus the resonance at 207.93 ppm is due to VECEX pentad and it shows correlations to $\alpha^C\beta^V$ protons at 2.38 ppm (cross peak w₃), $\alpha^C$ protons at 2.29 ppm (cross peak w₂) and $\alpha^V\beta^C$ protons at 1.80 ppm (cross peak w₁). The resonance at $\delta_C=207.62$ ppm is observed due to the occurrence of a C and a V next to E in the ECE triad and gives rise to CECEV pentad. The ketone carbonyl shows correlations to $\alpha^C\beta^C$ protons at 2.57 ppm (cross peak w₃) and $\alpha^C\gamma^V$ protons at 2.34 ppm (cross peak w'₂).

Correlations for ECV triads are observed at $\delta_C=205.95$ ppm in the HMBC spectrum. The ketone carbonyl carbon shows correlations to only the two diastereotopic protons at $\delta_H=2.52$ ppm, 2.66 ppm (cross peak v₁). These correlations are to the two non-equivalent $\alpha^C\alpha^V$ protons. Further correlations to methine proton were neither found in polymer with high vinyl acetate concentrations (Sample D) nor in the polymer with high carbon monoxide concentrations (Sample C).
Figure 3.17. Selected region from the 2D HMBC NMR spectra of sample A showing ketone carbonyl resonances.
Chain ends and Short chain branching (SCB): As the polymer is a terpolymer, various chain-ends are possible\textsuperscript{32}. In addition to that, methyl resonances due to short-chain branching (SCB) are also possible. McCord \textit{et al.} have studied SCB in E/V copolymers and identified the peak near 9.5 ppm in $^{13}$C spectra to the A$_3$B$_4^+$ structure. Others\textsuperscript{5,30} have studied E/CO copolymers and identified resonances from characteristic CO containing branches and ends. All the polymers studied here show three distinct peaks at $\delta_C=8.00$ppm, $\sim9.4$ppm and $\sim13.9$ppm (Figure 3.2) (positions slightly different in the spectra of individual samples may be due to the effect of adjacent groups); the intensities change depending on the concentration of the three monomers in the polymers. Figure 3.18 shows HSQC correlations from various chain ends observed in polyEVC (sample A) and HMBC correlations to the neighboring groups. The peak at $\delta_C=7.97$ppm and $\delta_H=1.00$ppm (cross peak CEc.e) in the HSQC spectrum is assigned to a CE branch end or chain end methyl group. It shows a correlation in the HMBC at $\delta_C=35.75$ppm (cross peak B$_2$ CEc.e) to the methylene carbon of the CE ethyl group, no correlation to the carbonyl carbon could be observed in the HMBC spectrum.

Correlations at $\delta_C=9.49$ppm and $\delta_H=0.86$ppm were observed in sample A are consistant with 1A$_3$B$_4^+$ and EVEc.e. This shows correlations to 2A$_3$B$_4^+$ carbon at 27.42 ppm and a weak correlation to the methine carbon at 74.15ppm (correlation observed only in sample D with highest amount of V). EVEc.e shows a correlation to the methine carbon at 75.53ppm (cross peak CH$_{EVE}$). Although the 1A$_3$B$_4^+$ peak is evident in the 1D spectra of all the polymers studied, the intensity is very low in Sample D with the highest percentage ($\sim55\%$) of vinyl acetate, while the intensity grows in polymers with the highest percentage of ethylene (Sample A and Sample B). This suggests the high amounts
of vinyl acetate in the backbone inhibits the backbiting reaction, either sterically or electronically or both.

The HSQC spectrum in Figure 3.18 also shows the cross peaks near 13.9ppm due to butyl branches ($B_5^+$, $B_4$, VEEc.e, CEEc.e, etc.). Correlations to various carbons and protons along the chain can be observed in the HMBC spectrum. Correlations to $2B_5^+$ and $3B_5^+$ can be observed at $\delta_C=22.69$ppm and $\delta_C=32.30$ppm, respectively. Correlations due to $B_4$ branch, $2B_4$ and $3B_4$ can be observed at $\delta_C=23.42$ppm and at $\delta_C=29.50$ppm in the HMBC spectrum.

![Diagram of polymer structure and NMR spectra](image)

Figure 3.18. Chain ends and short chain branches in sample A in HSQC and HMBC 2D NMR spectra.
3.3.3 Conclusions

A systematic study of four terpolymers with varying amount of monomers has confirmed the utility of using a variety of two-dimensional techniques in the polymer microstructure studies. The techniques were not only useful in the assignment of a range of major triad sequences, but were also useful in understanding stereochemistry in these sequences, which was not evident from one-dimensional techniques. Multiplicity selected gHSQC allowed separation and identification of methyl, methylene and methine resonances from each other; HSQC-TOCSY is a valuable adjunct to gHMBC, often giving information of two-bond correlations which are not evident in the gHMBC spectra. A few chain-ends and short-chain branching structures can also be identified from the 2D NMR experiments. In accordance to the study of EV polymers of McCord et al. no evidence was found for quaternary carbons, indicating that backbiting or chain transfer to the acetate methine does not occur. Although, it was possible to assign all the major triads, some resonances could not be assigned due to spectral overlap, hence work was continued using 3D-NMR with isotopic labeling to selectively study the resonances dispersed in the third dimension.

3.4 Characterization of Labeled Poly(ethylene-co-vinyl acetate-co-carbon monoxide)

Labeled poly(ethylene-co-vinyl acetate-co-carbon monoxide) (polyEV*C) was selectively labeled at the adjacent olefinic carbons of vinyl acetate to study the V-centered structures. 1D and 2D NMR experiments were initially used to confirm all the resonances and then 3D HC\textsubscript{A}C\textsubscript{X} and HC\textsubscript{A}C\textsubscript{X}-HH-TOCSY was used to study the V-centered structures.
3.4.1 1D and 2D NMR Studies

Figure 3.19 shows the $^{13}$C NMR spectra of the polyEV*C (Figure 3.19a), and polyEVC (Figure 3.19b). The $^{13}$C NMR spectrum of polyEV*C shows two major peaks, the $\alpha^V$ methylene peaks (~34 ppm) and the methine peaks (~74 ppm). The peaks are much enhanced compared to the NMR spectrum of polyEVC due to the $^{13}$C enrichment of the methine and the methylene carbons of vinyl acetate. As the sample quantity of the polyEV*C is less than the unlabeled polymer, the carbonyl carbon (204-212 ppm) resonances and the ester carbonyl carbon resonances (~169 ppm) were extremely low hence were not observed in the spectrum.

![Diagram of polyEV*C and polyEVC spectra](image)

**Figure 3.19.** 188.5 MHz $^{13}$C NMR spectra of a) polyEV*C and b) polyEVC (Sample C).
The expansions of the methine and the aliphatic regions of the spectra of polyEV*C (Figure 3.20a) and polyEVC (Figure 3.20b) are shown in Figure 3.20. The spectrum of labeled polymer (polyEV*C) shows all the resonances observed in the unlabeled polymer (polyEVC) with the exception that the resonances in polyEV*C are much broadened. This is due to the presence of $^{13}$C-$^{13}$C homonuclear couplings in the polymer from the uniformly labeled vinyl acetate. From the 1D spectrum it can be easily seen that the unambiguous assignment of the resonances is not possible and suggest the need to study the resonance assignment using nD-NMR.

![Figure 3.20. Expansions of aliphatic and methine regions from the 188.6 MHz $^{13}$C NMR spectra of a) polyEV*C and b) polyEVC (Sample C).](image)

Quantitative NMR Analysis: Quantitative NMR analysis of monomer composition was conducted on polyEV*C using $^1$H NMR. For monomer composition proton NMR is more useful due to its sensitivity, $^{13}$C NMR is less useful at this stage as the carbons of vinyl acetate are $^{13}$C enriched hence the signal originating form them
cannot be compared to other signals which are obtained from carbons at their natural abundance, whose resonances are barely detected here.

$^1$H NMR of the polymer shows three groups of resonances: the two resonances between 6.8 ppm to 5.8 ppm were assigned to $\alpha$-$\beta$ unsaturated ketone; groups of resonances from 5.3 ppm to 4.6 ppm were assigned to various methine protons; while the groups of resonances from 3.1 ppm to 0.6 ppm were assigned to various methylene and methyl protons. The resonances in these three areas were integrated.

The monomer composition was calculated by the same method as used for the unlabeled polyEVC samples. To calculate the amount of vinyl acetate in the polymer the integrated areas from methine resonances and the two resonances from $\alpha$-$\beta$ unsaturations were used as these areas purely represent the vinyl acetate derived units present in the polymer sample. Carbon monoxide amount in the polymer sample was calculated using two $\alpha^C$ methylene resonances, 3.1 ppm to 2.49 ppm ($\alpha^C\beta^C$) and 2.49 ppm to 2.12 ppm ($\alpha^C\delta^{+}/\alpha^C\gamma$). Column 3 of Table 3.4 shows the formulas used to calculate the mol % of each of the monomers of polyEV*C showed in column 4.

Table 3.5. Compositional analysis of polyEV*C using $^1$H NMR.

<table>
<thead>
<tr>
<th>monomer</th>
<th>integral range</th>
<th>formulas</th>
<th>mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.77-2.15</td>
<td>[C/4S]×100%</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>5.48-4.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>6.84-6.61</td>
<td>[V/S]×100%</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>6.21-5.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>[(T-6V)/4S]×100%</td>
<td></td>
<td>78</td>
</tr>
</tbody>
</table>

C = carbon monoxide  
V = vinyl acetate  
E = ethylene  
Us = $\alpha$-$\beta$ unsaturated ketone resonances  
T = total integral region = 4E + 6V+Us  
S = total numer of moles = (T+C-2V)/4
Figure 3.21 shows the expansions of the aliphatic region from the constant evolution time (CT) gHSQC 2D NMR spectrum of polyEV*C (Figure 3.21a) and correlations of the resonances two- three bonds away can be observed in gHMBC 2D NMR spectrum (Figure 3.21b). In the analysis of the labeled sample CT-gHSQC was used as it removes the $^{13}C-^{13}C$ coupling which would appear in the $f_1$ dimension of a standard gHSQC spectrum of this labeled polymer.

![Figure 3.21. Expansions from the aliphatic regions from 2D a) CT-HSQC and b) HMBC of polyEV*C.](image)

From the Figure 3.21a it can be observed that the major triads identified from the study of unlabeled polymer (polyEVC) can also be observed in the labeled polymer (polyEV*C). Experiments like HMBC and HSQC-TOCSY were used to confirm the resonance assignments which are summarized in Table 3.5. As the methylene and the methine carbons of vinyl acetate are labeled, the most intense resonances in the aliphatic
region are due to the $\alpha^V$ methylene protons and carbons, observed at $\delta_\text{H}= 1.33, 1.55$ ppm and $\delta_\text{C}= 34.5$ ppm. It can be observed from the CT-gHSQC spectrum that the $\alpha^V$ resonances are a cluster of resonances from many different possible V-centered triad sequences. 2D gHSQC, gHMBC and gHSQC-TOCSY study of polyEVC could be used to identify only few of the major triads among the twelve possibilities, due to a severe overlap in this region. This is due to the fact that the changes in $\alpha^V$ chemical shifts are very minor from the substitutions which are two-three bonds away. From HMBC spectrum of polyEV*C two major resonances could be identified in the corresponding region. Resonance at $\delta_\text{H}= 1.31, 1.53$ and $\delta_\text{C}= 34.60$ ppm in CT-HSQC spectrum shows correlations to protons at $\delta_\text{H}= 2.30$ ppm and protons at $\delta_\text{H}= 1.62$ ppm which suggest the CEVXX pentad ($\alpha^C\gamma^V = 2.30$ ppm, $\beta^V\beta^C = 1.62$ ppm); further correlations to protons at $\delta_\text{H}= 1.29$ ppm ($\delta^+\delta^-$) confirm the assignments of this set of resonances to CEVEE pentads.

The next correlation at $\delta_\text{H}= 1.51$ and $\delta_\text{C}= 34.16$ ppm in the CT-HSQC spectrum shows correlations to protons at $\delta_\text{H}= 2.30$ ppm ($\alpha^C\gamma^V$) protons at $\delta_\text{H}= 1.62$ ppm ($\beta^V\beta^C$) and correlations to two diastereotopic protons at $\delta_\text{H}= 1.77, 1.87$ ppm, which suggest assignment to CEVEC pentads although no correlations to the $\alpha^C\beta^V$ protons at $\delta_\text{H}= 2.39$ ppm was observed. This could be due to overlap with the $\alpha^C\gamma^V$ resonances. No correlations to the methine protons were observed in the HMBC spectrum for both the pentads.

The CT-HSQC spectrum of polyEV*C showed some additional resonances which were not detected in the corresponding spectra of unlabeled samples (polyEVC). For example, resonance at $\delta_\text{C}= 36.23$ ppm shows one bond correlations to the resonances of its
attached diastereotopic protons at $\delta_H=1.58$, 2.00 ppm in CT-HSQC. These resonances
did not show correlations in HMBC spectra but showed correlation at $\delta_H=4.96$ppm to
resonances of methine proton in the HSQC-TOCSY spectrum Figure 3.22. The chemical
shift calculations suggest that the resonance at $\delta_C=36.23$ppm in CT-HSQC experiment
could be from XVVCX pentads, but the assignment could not be confirmed using 2D
correlation experiments.

Figure 3.22. Expansions of aliphatic region of polyEV*C from 2D HSQC-TOCSY NMR
spectrum.

Figure 3.23 shows the expansions of methine regions from the CT-HSQC
spectrum (Figure 3.23a) and the HMBC spectrum (Figure 3.23b) of the polyEV*C. The
most intense resonance ($\delta_H=\sim4.87$ppm and $\delta_C=72-75$ppm) in CT-HSQC spectrum is
from XE/EX pentads and shows correlations to the methylene protons at $\delta_H=\sim2.36$ ppm,
$\delta_H=\sim1.77$ ppm and $\delta_H=\sim1.53$ ppm in the HMBC spectrum suggesting mainly XEVEC
pentads. From the HSQC-TOCSY spectrum (Figure 2.24) it can be observed that the
HSQC resonance at $\delta_C \approx 73.58$ ppm $\delta_H \approx -4.89$ ppm shows strong correlations to the proton resonances at $\delta_H = 2.37$ ppm, $\delta_H = 1.79$, 1.92 ppm, $\delta_H = 1.63$ ppm and $\delta_H = 1.55$ ppm, which suggests CEVEC pentad structures are the major structures present in the polymer. The chemical shifts cannot be accurately determined due to complications due to the $^{13}C-^{13}C$ couplings observed along the $f_1$ dimension of the HSQC-TOCSY spectrum.

Another group of resonances in the CT-HSQC spectrum (Figure 3.22) at $\delta_H = \sim 5.00$ ppm and $\delta_C = 70-72$ ppm are due the $m/r$ XVVEX pentads. These resonances failed to show conclusive structural evidence in HMBC spectra; hence, they were assigned based on the previous study of the unlabeled polymer (polyEVC). HSQC-TOCSY spectra (Figure 3.24) were again much more useful in the primary assignment of these resonances in the 2D study of polyEV*C. From Figure 3.24 it can be seen that only two strong sets of TOCSY resonances are present in the HSQC-TOCSY spectrum. The first group of resonances ($\delta_C = 71-72$ ppm, $\delta_H = 5.01$ ppm) which were assigned to $m$-XVVEX pentads as it shows TOCSY correlations to the two diastereotopic $\alpha^V \alpha^V$ protons at $\delta_H = 1.77$, 1.92 ppm and the second group of resonances ($\delta_C = 70-70.9$ ppm, $\delta_H = 5.03$ ppm) which were assigned to the $r$-XVVEX pentads as it shows TOCSY correlations to only a single proton resonance at $\delta_H = 1.78$ ppm. No further TOCSY correlations were observed but the assignment of $m/r$ resonances were confirmed unambiguously from the HSQC-TOCSY spectrum. Resonance assignments using 2D NMR are summarized in Table 3.5.
Figure 3.23. Expansions of methine regions of 2D a) CT-HSQC and b) HMBC of polyEV*C.

Figure 3.24. Expansions of methine region from 2D HSQC-TOCSY NMR of polyEV*C.
From the 2D NMR study of the labeled polyEV*C it can be easily observed that very little additional information could be attained especially in the $\alpha^V$ ($\sim$34 ppm) and the methine (70-74 ppm) regions of the spectra. Most resonance assignments could not be unambiguously determined due to severe overlap of resonances and $^{13}$C-$^{13}$C couplings in HSQC-TOCSY spectrum, or due to missing peaks in the HMBC spectrum. To alleviate this problem 3D NMR was be used. The vinyl acetate resonances were selectively enhanced and dispersed in a third dimension such that the overlapping resonances can be separated and assigned unambiguously depending on their methine carbon chemical shifts or $\alpha^V$ methylene carbon chemical shifts.
Table 3.6. Resonance assignment of polyEV*C using 2D NMR.

<table>
<thead>
<tr>
<th>carbon</th>
<th>polymer sequence</th>
<th>δ¹³C</th>
<th>δ¹H</th>
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<tbody>
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<td>0.88</td>
</tr>
<tr>
<td>1B₄</td>
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<td>CEV</td>
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</tr>
<tr>
<td>OCOCH₃</td>
<td>VEV</td>
<td>20.85</td>
<td>1.95</td>
</tr>
<tr>
<td>β⁺β⁺</td>
<td>VEV</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>β⁺δ⁺</td>
<td>ECE</td>
<td>24.08</td>
<td>1.54</td>
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<td>α⁺β⁺</td>
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<td>1.78,1.89</td>
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<tr>
<td>γδ⁺</td>
<td>CEE</td>
<td>29.65</td>
<td>1.25</td>
</tr>
<tr>
<td>δδ⁺</td>
<td>EEE</td>
<td>30.03</td>
<td>1.29</td>
</tr>
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<td>34.58</td>
<td>1.53,1.32</td>
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<td>CEV</td>
<td>33.91</td>
<td>1.56</td>
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<td>VVC</td>
<td>36.22</td>
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<td>VVV</td>
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<td>1.79,1.92</td>
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<td>α⁺γ⁺</td>
<td>CEV</td>
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<td>?</td>
<td>CVE?</td>
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<td>72-75</td>
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<td>VEV</td>
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</tr>
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<td>CH₇XEVE</td>
<td>CEV</td>
<td></td>
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<tr>
<td>CH₇XEVE</td>
<td>VEC</td>
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</tr>
<tr>
<td>CH₇XEVE</td>
<td>CEVEC</td>
<td>73.58</td>
<td>4.89</td>
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<table>
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<th>2D NMR</th>
<th>polyEV*C</th>
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<tr>
<td>δ¹³C</td>
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</tr>
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<tr>
<td>r-XVVE</td>
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</tr>
<tr>
<td>70-70.9</td>
<td>5.03</td>
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<tr>
<td>r-XVVE</td>
<td></td>
</tr>
<tr>
<td>?</td>
<td>5.03</td>
</tr>
</tbody>
</table>

Digital resolution, a₁ = 1.5 Hz/pt; b₂ = 1.8 Hz/pt.
3.4.2 3D NMR studies

Figure 2.5 and 2.6 (section 2.3.3) show the 3D gHCAC\textsubscript{X} and gHCAC\textsubscript{X}-HH-TOCSY sequences used to study this polymer. They work by sequential INEPT transfers from \(^1\text{H}\) to \(^{13}\text{C}_{\text{aliphatic}}\) (\(^{13}\text{C}_A\)) using one bond proton-carbon (\(^1\text{J}_{\text{CH}}\)) and then to \(^{13}\text{C}_{\text{methine}}\) (\(^{13}\text{C}_X\)), using one bond carbon-carbon couplings (\(^1\text{J}_{\text{CC}}\)). This is followed by \(t_1\) evolution period during which the encoding of \(^{13}\text{C}_X\) carbon chemical shifts takes place. A shifted laminar pulse was used in the middle of \(t_1\) evolution period to remove the couplings between \(^{13}\text{C}_A\) and \(^{13}\text{C}_X\). The magnetization is then transferred to \(^{13}\text{C}_A\) and then the evolution of the \(^{13}\text{C}_A\) chemical shifts takes place during the constant evolution time such that modulations due to couplings to all the other carbon atoms are removed. A reverse INEPT transfer from \(^{13}\text{C}_A\) to \(^1\text{H}_A\) is performed and then the antiphase magnetization created at the beginning of the sequence is refocused before detection of protons during \(t_3\). During the coherence transfer steps a WALTZ-16 decoupling sequence is used to decouple \(H_\alpha\) (\(^1\text{H}_A\)) protons. The carbon-carbon INEPT delays and the constant evolution time delays were optimized such that both EVE and EVV triads could be detected. Because the sequence uses relatively short coherence transfer delays (determined by large one-bond couplings) compared to the much longer coherence transfer delays in HMBC (determined by much smaller \(^2\text{J}_{\text{CH}}\)), there is less problem with loss of signal from rapid relaxation in these polymers. Thus, it is possible to see long-range structure correlations in the 3D spectra, which are absent from the HMBC spectra of these polymers.

To optimize the delays in the 3D experiment \(^{13}\text{C}\) enriched model compounds were used as the signals in a model compound are intense compared to the polymer samples studied. The model compounds studied were acetophenone selectively labeled at
carbonyl carbon and uniformly labeled propionic acid. There are four delays which should be optimized: first is the proton-carbon INEPT delay followed by $C_A-C_X$ INEPT delay, constant evolution time delay and the reverse INEPT delays. From the INEPT experiment it is known that the proton-carbon INEPT delay $\Delta_1 = 1/4J_{CH}$ for any molecule as each proton is attached to only one carbon and hence their multiplicity is two. Thus, it requires a total delay $2\Delta_1$ of $1/2J_{CH}$ to obtain antiphase magnetization at the end of the INEPT delay for the maximum polarization transfer to the carbon to take place. However, the reverse INEPT transfer delay needs to be optimized for each compound as the heteronucleus could be attached to one or more protons thus changing the multiplicity and hence the value of the optimum delay. For a CH unit, it has been determined that if a heteronucleus has one attached proton then the reverse-INEPT delay is the same as the INEPT delay i.e. $\Delta_2 = 1/4J_{CH}$ to refocus the magnetization, as in this case the multiplicity of the carbon from coupling to protons is also two. But, in case of a heteronucleus attached to two geminal protons theoretically it requires half as much time ($\Delta_2 = 1/8J_{CH}$) as that needed earlier and for a multiplicity of four i.e. three attached protons is requires ($\Delta_2 = 1/6J_{CH}$) to refocus the magnetization to obtain maximum signal. Also, all the components of the vector with multiplicity three cannot be refocused hence the compromise delay of $\Delta_2 = 1/6J_{CH}$ is used to obtain the best compromise signal from all three multiplets at the end of the sequence. It has also been determined that in case of one or more attached protons the recorded signal after a reverse-INEPT in a 2D experiment is actually one-half of the initial polarization$^{24}$. This is due to the fact that a single component is recorded. To overcome this problem and obtain higher sensitivity an additional reverse-INEPT sequence is added so that the orthogonal in-phase proton
magnetization components can be refocused and recorded. This method is helpful for heteronucleus with one attached proton while in the case of two or three protons attached to the heteronucleus there is no enhancement of signal. Applying these known concepts in case acetophenone the reverse-INEPT delay (multiplicity of carbon is four) was found to be $\Delta_2 = 1/6J_{CH}$ (based on $J_{CH} = 125$ Hz) while in case of uniformly labeled propionic acid it was found to be $\Delta_2 = 1/5J_{CH}$ (based on $J_{CH} = 130$ Hz). Acetophenone give the expected value but propionic acid gives a shorter delay value (expected delay of $1/8J_{CH}$, multiplicity of carbon is three). This could be due to the fact that all the carbons in propionic acid are labeled hence during the magnetization transfer an interference could be obtained from the -CH$_3$ group which has a multiplicity of four (expected delay value $1/6J_{CH}$). Hence, it can be concluded that the value deviated due to the –CH$_3$ group. Figure 3.25 and Figure 3.26 shows the optimization of INEPT and reverse-INEPT delays for acetophenone and propionic acid.

![Figure 3.25](image.png)

Figure 3.25. Optimization of delays: a) INEPT ($\Delta_1$) and b) reverse-INEPT ($\Delta_2$) delays in 3D HC$_A$C$_X$ NMR experiment of acetophenone $^{13}$C enriched at carbonyl carbon position.
Figure 3.26. Optimization of delays: a) INEPT ($\Delta_1$) and b) reverse-INEPT ($\Delta_2$) delays in 3D $H_C A C_X$ NMR experiment of uniformly labeled propionic acid.

The same consideration of multiplicity applies to optimization of the $C_A$-$C_X$ INEPT delays ($\tau_1$) as well as constant evolution time delay ($T$). In acetophenone the carbonyl carbon is $^{13}$C enriched ($C_X$) while the methyl carbon ($C_A$) is at its natural abundance. The multiplicity of $C_A$ during the $C_A$-$C_X$ INEPT is two hence the theoretical delay value is $1/4J_{CC}$ (based on $J_{CA-CX} = 42.8$ Hz). The optimization of the delay shows that the experimental value matches the theoretical value. In case of propionic acid all the carbons are $^{13}$C enriched; carbonyl carbon is $C_X$ while $-CH_2$ carbon is $C_A$. The multiplicity of $-CH_2$ carbon is three and hence the theoretical value for the $C_A$-$C_X$ INEPT is $1/8J_{CC}$ (based on $J_{CA-CX} = 55.3$ Hz), while the experimental value was observed to be twice of the expected value i.e. $1/4J_{CC}$. This discrepancy can be explained by looking at the $-CH_2$ region of the $^{13}$C spectrum closely. The carbon-carbon coupling of $-CH_2$ carbon to carbonyl carbon ($J_{CC} = 55.3$ Hz) and the $-CH_3$ ($J_{CC} = 34.8$ Hz) carbon is different it
appears as a doublet of doublet. Thus, in this case the multiplicity is no longer three but a combination due to two different couplings values.

The constant evolution time delay is the period during which the evolution of $C_A$ carbon takes place. The optimum evolution is also governed by the multiplicity of the $C_A$ carbons. Thus, in case of acetophenone the expected value of $n/4J_{CC}$, (based on $J_{CC} = 42.8$ Hz) where $n$ is an odd integer, was obtained. The $C_A$ carbon has one attached carbon ($C_X$) and hence the multiplicity is two. In case of propionic acid the multiplicity of $C_A$ again is determined by the $J_{CC}$, but in this case there is coupling to two different carbons $C_X$ and $-CH_3$ and hence the multiplicity and the optimum delay is governed by a combination of two couplings. Thus, propionic acid shows an optimum constant evolution time delay of $1/5J_{CC}$. Figure 3.27 and Figure 3.28 shows the calibration of $C_A$-$C_X$ INEPT and constant evolution time delays for acetophenone and propionic acid.

Figure 3.27. Calibration of delays: a) $C_A$-$C_X$ INEPT ($\tau_1$, ms) and b) constant time ($T$, ms) delays in 3D $HC_AC_X$ NMR experiment of acetophenone $^{13}$C enriched at carbonyl carbon position.
The polymer sample being studied here has a combination of structures which can be correlated to the study of model compounds. The $C_A-C_X$ INEPT delays and constant evolution time delays were both optimized to 6 ms ($1/4J_{CC}$) in the original $HC_AC_X$ experiment based on $^1J_{CC} = \sim 40$ Hz. But these delays were found to be inappropriate for the study of polyEV*C as it failed to show any correlation from the EVV fragments. Hence, they were optimized separately based on the multiplicity of the carbons (from coupling to adjoining carbons). This treatment was applied as both the adjacent carbons of vinyl acetate are $^{13}$C enriched and hence the magnetization evolves depending on the couplings to the neighboring $^{13}$C enriched carbons.

The evolution of magnetization in both EVE and EVV fragments is described as follows: in an isolated EVE fragment during the $C_A-C_X$ INEPT, the magnetization is
transferred from $C_A$ to $C_X$. The $C_A$ carbon has one neighbor which is 100% enriched and hence its multiplicity is two. The magnetization shows a doublet pattern and hence needs a time delay of $1/4J_{CC}$ ($J_{CC} = \sim 40$Hz) to produce antiphase magnetization needed to perform polarization transfer to $C_X$ to obtain a maximum signal. In an EVV fragment the splitting pattern is different; here the $\alpha^V\alpha^V$ $C_A$ carbon has two 100% enriched carbons as neighbors hence the multiplicity is three. In this situation the delay required is shorter than that needed for the EVE fragment. Thus, a delay of $1/8J_{CC}$ is required to obtain an antiphase condition to produce maximum polarization transfer.

The same principle is applied for the optimization of constant evolution time delay. During the constant evolution time, evolution of $C_A$ magnetization with coupling to adjoining ($C_X$) carbons takes place. Applying the same logic it can be deduced that an isolated EVE fragment requires a constant evolution delay of $n/2J_{CC}$ (where $n$ is an odd integer), where $n$ is an odd integer, to obtain a antiphase magnetization which can then be transferred to $H_A$ protons by reverse-INEPT. However, an EVV fragment with a multiplicity of three requires a delay of $n/4J_{CC}$ to obtain antiphase magnetization. As the EVV fragment was difficult to detect in the 3D experiment the delays were optimized so as to detect those fragments. Figure 3.28 shows the $f_2f_3$ slices from a truncated 3D $gHC_AC_X$ HH-TOCSY. Figure 3.29a shows one set of correlation near 33 ppm ($\alpha^V$) from the EVE fragment as the $C_A-C_X$ INEPT and constant evolution time delays were optimized to detect those fragments, while Figure 3.29b shows two set of correlations one near 33 ppm due to EVE fragments ($\alpha^V$) and an additional set of correlations near 39 ppm region ($\alpha^V\alpha^V$) as in this truncated 3D the previously mentioned delays were optimized to observe the correlations from EVV fragments.
Of all the possible triad sequences shown in Table 3.1 only V-centered triads need to be considered here as the vinyl acetate is labeled in the polymer. Of all the structures listed under V-centered triads some structures have a very low probability of occurrence due to steric and electronic influences on reactivity; these are shown with a slash across and are not considered here. The structures whose correlations are prominently detected are shown in red and these possible triad-centered-pentad structures are shown in Table 3.6 and are the only structures to be considered here.
Table 3.7. V-centered pentad sequences of polyEV*C.

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<th>% Probabilities*</th>
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*Based on E:V:C = 77.68:3.41:18.43

Triple resonance 3D gHC\(_A\)C\(_X\) and gHC\(_A\)C\(_X\)-HH-TOCSY can greatly simplify the overlapping regions by selecting the resonances for the structures with \(^{13}\)C- labeled V* units. The gHC\(_A\)C\(_X\) 3D experiment thus gives the connectivity information between H\(_A\), C\(_\text{methylene}\) (C\(_A\)) and C\(_\text{methine}\) (C\(_X\)) (as illustrated by the atoms highlighted in blue in Structure 3.3); while gHC\(_A\)C\(_X\)-HH-TOCSY 3D experiment gives correlation between this fragment and the neighboring protons in the same spin system in addition to the H\(_A\)–C\(_A\)–C\(_X\) connectivity (as illustrated by the atoms highlighted in green in Structure 3.3).

Scheme 3.3 Structural fragment of polyEV*C showing HC\(_A\)C\(_X\) connectivity information between H\(_A\), C\(_\text{methylene}\) (C\(_A\)) and C\(_\text{methine}\) (C\(_X\)) (in blue) and HC\(_A\)C\(_X\)-HH-TOCSY correlation from it to the neighboring protons in the spin system in addition to the H\(_A\)–C\(_A\)–C\(_X\) connectivity (in green).
The nomenclature used to present and analyze the 3D spectra is as follows: all the planes shown in the 3D HCACX and HCACX-HH-TOCSY are \( f_2f_3 \) planes at a selected \( f_1 \) frequency. Each \( f_2f_3 \) plane corresponds to the shift of a unique CHXVX chemical shift. Each HCACX correlation is labeled with a bold letter in red (\( a, b, c, \ldots \)) while pairs of correlations from the diasteoretopic protons are labeled as \( a, a'; b, b'; \ldots \). The TOCSY correlations to the protons in the same spin system are shown in bold black letters with numerical subscripts (\( a_1, a_2, a_3, \ldots \)). Thus, the HCACX spectrum gives \( ^1H-^{13}C_{\alpha}-^{13}CH \) connectivity information while HCACX-HH-TOCSY correlates this fragment to the neighboring protons which share \( ^1H-^1H \) couplings. The interpretation of the 3D-NMR data below is divided into two categories, EVE-centered structures and EVV-centered structures.

**EVE-Centered Structures.** Figure 3.30 shows the \( f_2f_3 \) slices from HCACX (Figure 3.30a) and the TOCSY correlations to the neighboring protons in HCACX-HH-TOCSY (Figure 3.30b) from the EEVEE pentad at \( f_1 = 74.05 \) ppm (methine carbon, \( C_X \)). The \( f_2f_3 \) slice from HCACX shows a unique \( H_{\alpha}-C_{\alpha} \) cross peak (\( a, a' \)) at \( \delta_{H} = 1.31, 1.54 \) ppm (nonequivalent protons) and \( \delta_{C} = 34.22 \) ppm from EEVEE pentad structures. The corresponding \( f_2f_3 \) slice from HCACX-HH-TOCSY at the same \( f_1 \) frequency shows TOCSY correlations to the methine proton (cross peak \( a_1 \)) at \( \delta_{H} = 4.92 \) ppm in addition to the \( H_{\alpha}-C_{\alpha} \) cross peak. Correlations to the \( \beta^V \) methylene protons (\( \delta_{H} = 1.33 \) ppm) appear at a chemical similar to that of the \( \alpha^V \) proton resonances (\( \delta_{H} = 1.31 \) ppm) and contribute to the intensity of \( a' \) as they fall very close to each other. As EEVEE is a symmetric pentad no other correlations could be observed in the HCACX-HH-TOCSY spectrum.
Figure 3.30. \( f_2 f_3 \) slices from 3D HC\( \Delta \)C\( \chi \) (a) and HC\( \Delta \)C\( \chi \)-HH-TOCSY (b) showing correlation from EEVEE at \( f_1 = 74.05 \) ppm.

The variation of environment around the \( C_\Lambda \) carbons in a pentad changes the \( ^{13}C \) chemical shifts of the cross peaks. Thus, replacing one of the Es with a V gives rise to a VEVEX pentad with a new set of crosspeaks at \( f_1 = 73.86 \) ppm (Figure 3.30). The HC\( \Delta \)C\( \chi \) \( f_2 f_3 \) slice (Figure 3.31a) shows the \( H_\Lambda -C_\Lambda \) correlation (b, \( b' \)) at \( \delta_H = 1.31, 1.54 \) ppm (nonequivalent protons) and \( \delta_C = 34.14 \) ppm. These cross peaks show correlations to the \( \beta^V \beta^V \) methylene protons at \( \delta_H = 1.39 \) ppm (cross peaks \( b_1 \)) and another correlation to the methine proton at \( \delta_H = 4.90 \) ppm (cross peak \( b_2 \)) in the plane with the same \( f_1 = 73.86 \) ppm.
ppm chemical shift in HC\textsubscript{A}C\textsubscript{X}-HH-TOCSY spectrum (Figure 3.31b). Thus, it can be confirmed that the V of EVE triad is the near another V unit. But the environment on the other side of the VEVEX could not be confirmed as no additional correlations could be observed clearly in the HC\textsubscript{A}C\textsubscript{X}-HH-TOCSY spectrum. The presence of a C gives rise to some unique resonances and hence that possibility was discarded hence it can be concluded that these correlations can be attributed to VEVEV or VEVEE pentads.

Figure 3.31. \(f_2f_3\) slices from 3D HC\textsubscript{A}C\textsubscript{X} (a) and HC\textsubscript{A}C\textsubscript{X}-HH-TOCSY (b) showing correlation from VEVEE at \(f_1 = 73.86\) ppm.

If V in VEVEE is replaced by C to form a CEVEE pentad, the C\textsubscript{A} resonance is shifted upfield as seen in HC\textsubscript{A}C\textsubscript{X} slice at \(f_1 = 73.72\) ppm (Figure 3.32a). The cross peak c
is the H\textsubscript{A}-C\textsubscript{A} correlation of CEVEE pentads in the HC\textsubscript{A}C\textsubscript{X} spectrum. The TOCSY correlations corresponding to this structure can be observed in the Figure 3.32b. Cross peaks c\textsubscript{1} (\(\delta\text{H} = 1.63\) ppm) can be assigned to \(\beta^V\beta^C\) protons, cross peak c\textsubscript{2} to \(\alpha^C\gamma^V\) protons (\(\delta\text{H} = 2.33\) ppm) and cross peak c\textsubscript{3} to CH\textsubscript{EVE} protons of CEVEE pentads. Correlations to the CEV triad are very clearly visible along with those of the VEE triad in a CEVEE pentad as the all the \(\alpha\)-proton correlations fall around 1.56 ppm and thus are overlapping. The HC\textsubscript{A}C\textsubscript{X} and HC\textsubscript{A}C\textsubscript{X}-HH-TOCSY slices show some additional resonances between \(\delta\text{C} = 34-35\) ppm regions; these are the residue of correlations bleeding through from the adjoining slices. As the difference between two consecutive slices is about 0.024 ppm the resonances from adjoining slices sometimes bleed through and can be observed in the slice presented.
Figure 3.32. $f_2 f_3$ slices from 3D HC$_{\alpha C X}$ (a) and HC$_{\alpha C X}$-HH-TOCSY (b) showing correlation from CEVEE at $f_1 = 73.72$ ppm.

A different EVE triad can be formed by placing the C unit on the opposite side of the pentad to form and EEVEC pentad. The 3D correlations of such a pentad can be seen in Figure 3.33. Figure 3.33a shows $f_2 f_3$ plane of XXVEC pentad at $f_1 = 73.58$ ppm from HC$_{\alpha C X}$ spectrum. The plane shows cross peaks $d$, $d'$ due to nonequivalent protons H$_A$ protons at $\delta_H = 1.50$, 1.55 ppm and C$_\alpha$ at $\delta_C = 34.30$ ppm. TOCSY cross peaks from HC$_{\alpha C X}$-HH-TOCSY spectrum, due correlations with the neighboring protons are shown in Figure 3.33b. The correlations to VEC triad of the pentad part are shown by cross peaks $d_2$, $d'_2$ ($\delta_H = 1.80$, 1.92 ppm) which correspond to the $\alpha^V \beta^C$ nonequivalent protons.
A very weak correlation could be observed to the $\alpha^C\beta^V$ protons at $\delta_H = 2.40$ ppm (cross peak $d_3$). A correlation at $\delta_H = 4.90$ ppm (cross peak $d_4$) corresponds to the correlation with the methine proton resonance. Another correlation is observed at $\delta_H = 1.30$ ppm (cross peak $d_1$) which corresponds to a correlation with the resonance of $\beta^V\gamma^+$ protons and thus an ethylene environment is confirmed on the left side of the XXVEC pentad indicating the EEVEC pentad.

Figure 3.33. $f_2f_3$ slices from 3D HCA$_X$ (a) and HCA$_X$-HH-TOCSY (b) showing correlation from EEVEC at $f_I = 73.58$ ppm.
Another set of correlations from unique pentad was observed at $f_1 = 73.16$ ppm in the 3D-NMR spectra as can be seen in Figure 3.34. The $f_2f_3$ plane from the HC$_A$C$_X$ spectrum (Figure 3.34a) shows an H$_A$–C$_A$ correlation at $\delta_H = 1.54$ ppm and $\delta_C = 33.87$ ppm (cross peak e). Figure 3.34b shows the TOCSY correlations in the HC$_A$C$_X$-HH-TOCSY slice. Cross peak e$_1$ corresponds to $\beta^V\beta^C$ ($\delta_H = 1.61$ ppm); cross peak e$_3$ corresponds to $\alpha^C\gamma^V$ ($\delta_H = 2.31$ ppm). Both these correlations suggest the presence of a CEV triad on the left side of the pentad structure. Cross peaks e$_2$, e'$_2$ correspond correlations with the nonequivalent $\alpha^V\beta^C$ protons ($\delta_H = 1.79$, 1.90 ppm) while a weak correlation was observed at $\delta_H = 2.37$ ppm (cross peak e$_4$) corresponds to a correlation with $\alpha^C\beta^V$ proton resonances, suggesting the presence of a VEC triad on the right side of the pentad. Thus, the cross peaks in the 3D planes shown in Figure 3.34 represents CEVEC pentads. A methine correlation (CH$_{EVE}$) was also observed at $\delta_H = 4.89$ ppm shown by e$_5$. 
Figure 3.34. $f_2 f_3$ slices from 3D HC$_A$C$_X$ (a) and HC$_A$C$_X$-HH-TOCSY (b) showing correlation from CEVEC at $f_1 = 73.16$ ppm.

**EVV-Centered Structures.** The EVV-centered structures display stereosequence effects from (m/r structures) as well as monomer sequence effects for the resonances of $\alpha^V \alpha^V$ protons. Additionally, two adjacent vinyl acetate units are labeled so two sets of resonances can be observed in HC$_A$C$_X$ slices and correlation among these two sets of resonances can be used to interpret and confirm the nature of the triad structures on both sides of the center V units in pentads.
From the 2D CT-HSQC NMR studies it was confirmed that two sets of resonances are observed in the methine carbon region of EVV triad resonances and they were confirmed to be due to $m$- and $r$-EVV triad structures. Although, these resonances could be easily observed in the 2D CT-HSQC, each resonance in the group could not be assigned to specific higher n-ads. The $f_1f_3$ truncated 3D also showed two groups of resonances with each group containing two resonances. The first group was assigned to $m$-EVV triads and was observed at $\delta_C = 71.22$ ppm and $\delta_C = 70.91$ ppm while the second group was assigned $r$-EVV triads and was observed at $\delta_C = 70.39$ ppm and $\delta_C = 70.05$ ppm.

Figure 3.35 shows the $f_2f_3$ plane at $f_1 = 71.23$ ppm from the $HC_A C_X$ 3D spectrum (Figure 3.35a) and the corresponding $f_2f_3$ plane from the $HC_A C_X$-HH-TOCSY 3D spectrum (Figure 3.35b). The $f_2f_3$ planes from $HC_A C_X$ spectrum shows two sets of $H_A - C_A$ cross peaks; $f$ at $\delta_H = 1.60$ ppm, $\delta_C = 34.39$ ppm and $g$, $g'$ at $\delta_H = 1.79$, 1.93 ppm (nonequivalent protons), $\delta_C = 38.92$ ppm. Cross peak $f$ corresponds to the $\alpha^V \delta^+$ resonance while cross peak $g$, $g'$ corresponds to the $\alpha^V \alpha^V$ resonance. The cross peak $f$ shows TOCSY correlation cross peak $f_1$ at $\delta_H = 1.32$ ppm corresponding to $\beta^V \delta^+$ type protons and to $f_2$ at $\delta_H = 5.02$ ppm which represents methine ($CH_{EVV}$) protons. Thus, this EVV triad exists in an EEVVX pentad. The second set of correlations identifies the right side (VVX triad). The $g$, $g'$ cross peaks due to nonequivalent $\alpha^V \alpha^V$ protons show TOCSY correlations at $g_1$ to the $\beta^V \delta^+$ protons, to $\alpha^V \delta^+$ protons at $g_2$ and finally to the methine proton ($CH_{VVE}$) at $g_3$. As no other unique correlation was observed these cross peaks were assigned to $m$-EEVVE pentads. The meso structure was also confirmed due to the
presence of nonequivalent $\alpha^V\alpha^V$ protons resonances. Although, the cross peak $g, g'$ of $\alpha^V\alpha^V$ protons show correlations to the $\alpha^V\delta^+$ protons at $g_2$ no correlations were observed from $\alpha^V\delta^+$ (cross peak $f$) to the $\alpha^V\alpha^V$ protons in HC$_A$C$_X$-HH-TOCSY. This could be due to the fact that $\alpha^V\alpha^V$ proton resonances are weak due to nonequivalence and the presence of geminal and numerous vicinal couplings.

Figure 3.35. $f_2f_3$ slices from 3D HC$_A$C$_X$ (a) and HC$_A$C$_X$-HH-TOCSY (b) showing correlation from $m$-EEVVE at $f_1 = 71.23$ ppm.

Figure 3.36 shows the correlations from $m$-CEVVE pentads. Figure 3.36a shows HC$_A$C$_X$ correlations at $f_1 = 70.86$ ppm and the corresponding HC$_A$C$_X$-HH-TOCSY
correlations can be observed in Figure 3.36b. The cross peak h in HCACX spectrum corresponds to the $\alpha^V\gamma^C$ protons ($\delta_H = 1.58$, $\delta_C = 33.96$ ppm) and shows TOCSY correlations to one of the nonequivalent $\alpha^V\alpha^V$ protons at h₁ ($\delta_H = 1.96$ ppm), to unique $\alpha^C\gamma^V$ resonances at h₂ ($\delta_H = 2.34$ ppm) and to the methine proton (CHEVV) at 4.99 ppm (cross peak h₃). While the $\alpha^V\alpha^V$ HCACX resonances (cross peaks i, i') observed at $\delta_H = 1.79, 1.94$ ppm and $\delta_C = 38.89$ ppm shows correlations to the $\alpha^V\gamma^C$ protons (cross peak i₁) at $\delta_H = 1.58$ ppm and a correlation to the methine proton was observed at $\delta_H = 4.99$ ppm (cross peak i₂). No TOCSY correlation to the $\alpha^C\gamma^V$ protons was observed from the cross peak i, i'; this could be due to a non-optimal mix time (50ms) used in the sequence.
Figure 3.36. $f_2 f_3$ slices from 3D HC$_A$C$_X$ (a) and HC$_A$C$_X$-HH-TOCSY (b) showing correlation from m-CEVVE at $f_1 = 70.86$ ppm.

Figure 3.37 shows the $f_2 f_3$ plane from the HC$_A$C$_X$ spectrum (Figure 3.37a) at $f_1 = 70.34$ ppm. This slice shows the two sets of H$_A$–C$_A$ resonances designated by the cross peaks $j$ and $k$. Cross peak $j$ ($\delta_H = 1.56$ ppm, $\delta_C = 34.81$ ppm) shows correlations to $j_1$ at $\delta_H = 1.31$ ppm ($\beta^V \delta^+ \alpha$ protons), to $j_2$ at $\delta_H = 1.78$ ppm ($r-\alpha^V \alpha^+$ protons) and $j_3$ at $\delta_H = 5.03$ ppm in $f_2 f_3$ HC$_A$C$_X$-HH-TOCSY slice (Figure 3.37b). These correlations can be attributed
to EEVVX pentad. The \( k \) cross peak is due to the \( r-\alpha^V \alpha^V \) resonance (\( \delta_H = 1.78 \text{ ppm}, \delta_C = 38.89 \text{ ppm} \)) and shows TOCSY correlations to the \( k_1 \) at \( \delta_H = 1.31 \text{ ppm} \) (\( \beta^V \delta^+ \) protons), \( \alpha^V \delta^+ \) protons at \( \delta_H = 1.56 \text{ ppm} \) (cross peak \( k_2 \)) and to the methine proton at \( \delta_H = 5.03 \text{ ppm} \) (cross peak \( k_3 \)). A correlation was observed at \( \delta_H = 1.72 \text{ ppm} \) in the HC\( A_C_X \) slice which could not be assigned using HC\( A_C_X \)-HH-TOCSY. From the correlations observed in HC\( A_C_X \)-HH-TOCSY the pentad are attributed to \( r\)-EEVVE.

![Diagram of the molecular structure and correlations](image)

Figure 3.37. \( f_2f_3 \) slices from 3D HC\( A_C_X \) (a) and HC\( A_C_X \)-HH-TOCSY (b) showing correlation from \( r\)-EEVVE at \( f_1 = 70.34 \text{ ppm} \).
Figure 3.38a shows $f_2f_3$ planes from the HC$_A$C$_X$ and HC$_A$C$_X$-HH-TOCSY 3D spectra at $f_1 = 70.06$ ppm of $r$-CEVVE pentad structure. Cross peak $l$ at $\delta_H = 1.60$ ppm $\delta_C = 34.39$ ppm in HC$_A$C$_X$ shows TOCSY correlations (Figure 3.38b) to the $r\alpha^V\alpha^V$ protons at $\delta_H = 1.79$ ppm (cross peak $l_1$), to the unique $\alpha^C\gamma^V$ protons at $\delta_H = 2.35$ ppm (cross peak $l_2$) and to the methine proton at $\delta_H = 5.03$ ppm (cross peak $l_3$). The cross peak $l_2$ confirms the presence of C unit at $\gamma$ position from the $\alpha^V$ of vinyl acetate group. The $r\alpha^V\alpha^V$ cross peak $m$ ($\delta_H = 1.79$ ppm, $\delta_C = 38.89$ ppm) in HC$_A$C$_X$ slice shows correlations to the $\alpha^V\gamma^C$ protons at $\delta_H = 1.60$ ppm (cross peak $m_1$) and to the methine proton at $\delta_H = 5.03$ ppm (cross peak $m_2$). No further correlations were observed. This HC$_A$C$_X$ slice from an $r$-CEVVE pentad also shows two other resonances at $\delta_H = 1.60$ ppm and $\delta_H = 1.73$ ppm which could not be assigned using HC$_A$C$_X$-HH-TOCSY experiment.
Figure 3.38. $f_2f_3$ slices from 3D HC$_A$C$_X$ (a) and HC$_A$C$_X$-HH-TOCSY (b) showing correlation from $r$-CEVVE at $f_1=70.06$ ppm.

The resonances assignments of $\alpha^V/\alpha^V/\alpha^V$ carbon/protons and the various methine carbon/protons at pentad levels are summarized in Table 3.7. From the 3D HC$_A$C$_X$ and HC$_A$C$_X$-HH-TOCSY spectra it can be seen that it was possible to assign the resonances of at least five different types of pentad EVE centered pentads and the resonances of at least two different $m$- and $r$- EVV centered pentads which could not be separated in the 2D NMR spectra due to severe overlap.
Table 3.8. Resonance assignment of polyEV*C using 3D NMR.

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$^a$Digital resolution $f_1 = 2.2$ Hz/pt, $f_2 = 3.6$ Hz/pt

$^b$Digital resolution $f_3 = 1.3$ Hz/pt.

3.4.3 Conclusions

The 2D NMR studies of the labeled polyEV*C confirmed the triad resonances which were assigned in the unlabeled polyEVC. Also, the experiments were useful to confirm the $m$- and $r$-triads in the EVV methine resonance regions. However, due to $^{13}C$-polymer sequence $\delta^{13}C$ and $\delta^1H$. 

$^{13}$C couplings or cancellation of antiphase components of the correlation in the 2D experiments, they could not be used for the complete resonances assignments of the triads. The 3D NMR experiments greatly simplified the overlapping resonances by dispersing them into third dimension such that the resonances arising from various V-centered triads could be identified and assigned up to pentad levels by simple inspection of the resolved cross peak patterns. Optimization of the $^{13}$C–$^{13}$C INEPT delays assisted the detection and identification of low concentration EVV-triads and thus helped in the assignment of $m$- and $r$- EVV triads up to pentad levels. Thus it can be seen that the gHC$_A$C$_X$ and gHC$_A$C$_X$-HH-TOCSY 3D NMR experiments can be used as complimentary experiments and can be successfully implemented for structure elucidation of complex molecules.
CHAPTER IV
CHARACTERIZATION OF LABELED POLY(ETHYLENE-CO-1-HEXENE-CO-CARBON MONOXIDE)

4.1 Introduction

α-Olefins such as 1-butene, 1-hexene or 1-octene are important commercial monomers used to control the density of polyethylene. By varying the amount of these monomers incorporated into polyethylene, it is possible to reduce the density of the copolymers such that commercial polyethylenes known as linear low-density polyethylenes (LLDPE) are produced. The physical and mechanical properties, crystallinity of the polyethylene are highly dependent on the monomer introduced. When 1-hexene is copolymerized with ethylene butyl branches are introduced along the polymer backbone. These branches in the polymer influence its processing properties. The properties like melting temperature or crystallization behavior can be altered or fine-tuned by changing the 1-olefin monomer or its concentration or by changing the catalyst used yielding products with wide range of applications. Due to the increased significance in commercial fields these polymers were extensively investigated using various NMR techniques.17, 22, 52-54
Polyketones are another class of materials which belong to high performance thermoplastic polymer family. The ketonic group introduces a polar group in the polymer backbone which makes polymers which are extremely resistant to solvent and have high melting points and good mechanical properties. Despite their strength due to the high crystallinity these polymers are brittle hence to decrease the crystallinity of the polymers propylene was polymerized with ethylene and carbon monoxide\textsuperscript{55}. Introduction of methyl group decreases the crystallinity and melting point of polymer but also makes its stronger and less brittle.

A polymer with similar monomers is being studied here. The polymer is a terpolymer of ethylene (E), 1-hexene (H) and carbon monoxide (C) in which the ketone carbonyl carbon of carbon monoxide is $^{13}$C enriched. The polymer is prepared with high concentration of C to achieve an alternating polymer, as it is known that under such conditions C forms alternating sequences with another monomer in a polymer chain when present in high amount. For the primary assignment of resonances in the polymer 1D and 2D NMR was used and finally 3D NMR experiments were used to obtain information of C-centered structures as the polymer is $^{13}$C enriched at C positions.

4.2 Experimental

The polymer was synthesized and NMR sample was prepared and provided by the group of V. Busico at the University of Naples, Italy. 1D proton/carbon and 2D HSQC and HMCB NMR experiments were used initially to identify the C-centered resonances and then 3D HCA$C_X$ and HCA$C_X$-HH-TOCSY NMR experiments were used for the final analysis.
4.2.1 Preparation of labeled Poly(ethylene-co-1-hexene-co-carbon monoxide) for NMR analysis.

The polymer sample was prepared and provided by group of V. Busico at the University of Naples, Italy. CDCl₃ was used as the solvent for the preparation of polymer solution. Tetramethylsilane (TMS) was added in trace quantity to serve as an internal chemical shift reference in both the 1D, 2D and 3D NMR spectra.

4.2.2 Acquisition of 1D NMR

The 1D $^1$H NMR spectrum of labeled sample was acquired with the following parameters: a $\pi/2$ pulse of 7.1 $\mu$s; 2.8 kHz spectral width; 32 transients, 2.5 s acquisition time and a 4 s relaxation delay for quantitative analysis. The data were zero filled to 256 k and exponentially weighted with 0.5 Hz line-broadening before Fourier transformation.

The quantitative 1D $^{13}$C NMR experiment was performed on the labeled polymer sample using following parameters: a $\pi/2$ pulse of 6.75 $\mu$s; 47.2 kHz spectral width; 1024 transients. 1.4 s acquisition time and a 25 s relaxation delay (carbonyl carbons had longest $T_1$ of 4-5s) for quantitative analysis. Spectra were obtained using WALTZ-16 gated decoupling to suppress nuclear Overhauser effect (NOE); 132k data points were acquired for each fid and then the data were zero filled to 256 k and exponentially weighted with 0.5 Hz line-broadening before Fourier transformation.
4.2.3 Acquisition of 2D NMR Spectra

Heteronuclear single quantum correlation (gHSQC) and heteronuclear multiple quantum (gHMBC) experiments were collected on the 750 MHz spectrometer using a $^1\text{H}/^1\text{H}/^1\text{H}^\text{15N}$ 5mm cryoprobe.

gHSQC spectra was collected with following parameters: The $\pi/2$ pulse widths for $^1\text{H}$ and $^1\text{C}$ were 8.5 $\mu$s and 15.0 $\mu$s, respectively. Data were acquired using the following parameters: relaxation delay 1 s, the delay $\Delta$ set to $1/(2\times^1J_{CH})$, ($^1J_{CH}$ =$130$ Hz) to optimize the intensities of cross-peaks from one bond $^1\text{H}-^1\text{C}$ correlations, and an acquisition time of 0.128 s with simultaneous $^1\text{C}$ GARPI$^{39}$ decoupling; 8 transients were averaged for each of $2\times1024$ increments during $t_1$ for phase sensitive detection based on the States method.$^{40}$ The evolution time was incremented to provide the equivalent of 7.5 kHz spectral window in the $f_1$ dimension and 8.0 kHz spectral window was used in the $f_2$ dimension. The encoding and the decoding gradient pulses were 0.219 T/m and 0.109 T/m, with 2.0 ms and 1.0 ms durations, respectively. Linear prediction was used to forward extend the data two- to four-times its original length, to compensate for the short acquisition time as well as the relatively small number of points sampled in the evolution time dimension. Data were zero filled to provide a $4096\times4096$ matrix and processed with sinebell and shifted sinebell weighting functions before Fourier transformation.

The HMBC spectrum of the labeled polymer was acquired using same parameters. The data was acquired with 80.0 ms $\tau$ delay (set to $1/(2\times^3J_{CH})$) to optimized for two- and three-bond $^1\text{H}-^1\text{C}$ correlations, a relaxation delay of 1.0 s, a 0.128 s acquisition time, a delay $\Delta$ set to $1/(2\times^1J_{CH})$ ($^1J_{CH}$ =$130$ Hz) for suppressing the 1-bond
$^1$H-$^{13}$C correlations. The $^1$H and $^{13}$C $\pi/2$ pulse widths used to obtain the spectrum were 8.5\,µs and 15\,µs, respectively. The coherence selection between $^1$H and $^{13}$C was achieved using two 2.0 ms gradient pulses with strengths of 0.219 T/m and 0.164 T/m; 16 transients were averaged for each of 1024 $t_1$ increments. The evolution time was incremented to provide the equivalent of 3.8 kHz spectral widths in the $f_1$ dimensions and 8.0 kHz spectral width in the $f_2$ dimensions. Data were zero filled to provide a 4096$\times$4096 matrix and processed with sinebell and shifted sinebell weighting functions before Fourier transformation.

4.2.4 Acquisition of 3D NMR

The 3D analysis of labeled sample was conducted using two 3D NMR experiments: $g$HC$_A$C$_X$ and $g$HC$_A$C$_X$-HH-TOCSY. The 3D spectra were collected using the two channel version of the pulse sequences.

The 3D $g$HC$_A$C$_X$ NMR spectrum was collected using following parameters: The $\pi/2$ pulses for $^1$H and $^{13}$C were 7.0\,µs and 12\,µs, respectively. The spectral width of 1508.3, 1697.8 and 900.1 were used along $f_1$, $f_2$ and $f_3$ dimensions. The spectra were acquired using following acquisition parameters: a relaxation delay of 1s, a delay $\Delta$ of 2.0 ms ($1/4^{1}J_{CH}$, where $^{1}J_{CH} = 130$Hz), a delay $\tau_1$ of 6.0 ms ($1/4^{1}J_{CC}$, where $^{1}J_{CC} = 40$Hz) and a constant evolution time delay $T$ of 6.0ms ($1/4^{1}J_{CC}$, where $^{1}J_{CC} = 40$Hz) followed by a 0.086s of acquisition time with GARP1 decoupling; 32 transients were averaged for each of $2 \times 32$ increments during $t_1$, $2 \times 20$ increments during $t_2$, and a total of 154 points in $t_3$. A shifted laminar pulse$^{43}$ was used for the off-resonance selective excitation of the methine carbon region (164.46 ppm away from the carbon transmitter). This was
achieved by setting the carbon transmitter at 47.58 ppm and then by using the “make180C_CO” macro in Varian’s ProteinPack software. The selective π/2 13C pulses were calculated using the formula: \(\sqrt{\frac{15}{4} \times dfrq \times (\text{offset difference between aliphatic (47.58 ppm) and carbonyl carbon (212.04 ppm) regions})}\), where dfrq is the 13C decoupler frequency. To decouple the protons during the transfer of magnetization from \(C_A\) to \(C_X\), \(t_1\) evolution and during the constant time period, the WALTZ-16 decoupling sequence with \(\gamma B_1 = 7.5 \text{ kHz}\) was used. The \(^1H-^{13}C\) coherence transfer was accomplished by gt6 (1.6ms) and gt9 (0.4ms) field gradients of strength 0.28 T/m. The other pulse gradients were of following strength and duration: \(g_1 = 0.30 \text{ T/m and 1.0 ms}, g_2 = 0.17 \text{ T/m and 0.75 ms}, g_3 = 0.32 \text{ T/m and 1.0 ms}, g_4 = 0.21 \text{ T/m and 0.30 ms}, g_5 = 0.17 \text{ T/m and 0.20 ms}, g_7 = 0.17 \text{ T/m and 1.0 ms}, g_8 = 0.28 \text{ T/m and 0.80 ms}\). Quadrature detection in the \(t_1\) (13C\_chemical shift) dimension was achieved by alternating the phase of \(\phi_1\) in a States-TPPI manner\(^{44}\). Echo/anti-echo selection in the \(t_2\) (13C\_chemical shift) dimension was achieved by inverting the amplitude of the g6 gradient pulse and the phase \(\phi_4\)^{45}. The total experimental time was 27 h. The data were processed using Varian’s VNMR software using \(f1\text{coef} = ‘1, 0, 0, 0, 0,-1, 0’\) and \(f2\text{coef} = ‘1, 0, -1, 0, 0, -1, 0, -1’\). The raw data were linear predicted to two times the number points sampled in \(t_1\) and \(t_2\) dimensions, zero-filled to give a \(512 \times 512 \times 4096\) matrix and then weighted with sinebell and shifted sinebell functions before Fourier transformation.

The 3D gHC\(_A\)C\(_X\)-HH-TOCSY NMR spectrum was collected using the same parameters described above for gHC\(_A\)C\(_X\) NMR except the spectral width along \(f_3\) dimension was 1951.0 Hz to observe all the TOCSY correlation. The TOCSY isotropic mixing time was 60 ms and was achieved using DIPISI-2\(^{46}\) mixing sequence of strength.
γB_H = 7 kHz. The data were linear predicted to 2 times the number points sampled in t_1 and t_2 dimensions, zero-filled to give a 512 × 512 × 4096 matrix and then weighted with sinebell and shifted sinebell functions before Fourier transformation.

4.3 Characterization of polyEH*C* by multidimensional NMR

Poly(EHC*) was synthesized with the aim to characterize the different C-centered structures. 1D proton/carbon and 2D gHSQC/gHMBC experiments were initially used to identify the resonances. 3D HCX and HCX-HH-TOCSY were used finally to reveal connectivity information.

The structures of interest for this study are the C-centered structures as the ketone carbonyl carbons are^{13}C enriched in this polymer. The polymer was synthesized with high percentage of carbon monoxide so that an alternating sequence of C and E/H is formed. Thus, structures formed in this case are not categorized into possible triads depending on the monomer as done before for polyEVC. Here, each pair of monomers can be considered as a pseudo monomer e.g. EC or HC as each H/E unit is followed by a C. Thus, monomer sequence can be treated as a pseudo-triad of six monomers or as a pseudo-tetrad of eight monomers.

The nomenclature used to identify each carbon atom in the structures in polyEH*C* is the same as that used for polyEVC. Some of the structures of polyEH*C* are shown in Scheme 4.1. Superscript ‘H’ or ‘C’ is used to define the branch formed by 1-hexene or carbon monoxide units, respectively. For example, the carbon adjacent to carbonyl carbon on one side and adjacent to methine carbon bearing –C_4H_9 side chain is labeled \( \alpha^C \alpha^H \) as it is \( \alpha \) to a carbonyl carbon and also \( \alpha \) to the methine carbon bearing –
C₄H₉ side chain. The methine resonances are labeled as ‘CH’. Carbons in all the other triads are indicated in similar fashion. The carbons in –C₄H₉ hydrocarbon chain branch are defined by iBₙ, where ‘i’ designates the position in the branch, starting from the methyl group in position ‘1’, and ‘n’ gives the length of that branch.

Scheme 4.1. Structures and nomenclature for polyEHC* triads.

4.3.1 1D NMR Analysis and Quantitative Study.

Figure 4.1a shows the full proton spectrum of polyEHC*. Two separate groups of resonances can be observed in the spectrum, the group of resonances from 0.72 ppm to 1.62 ppm is due to methyl and methylene protons from the butyl branch of 1-hexene. The 1B₄ methyl protons are observed at ~0.8 ppm, 2B₄ and 3B₄ methylene protons were observed at ~1.2 ppm. The 4B₄ protons were observed to be non-equivalent and one of the 4B₄ protons was also observed at ~1.2 ppm while the other one is observed near 1.5 ppm. The group of resonances from 2.21 ppm to 2.99 ppm is due to protons α to carbonyl groups. Figure 4.1b shows the expansion of the αC proton resonances. The tallest peak in
the group is due to $\alpha^C\delta^+$ protons ($\delta_H = 2.62$ ppm). The methylene protons from CHC sequence are diastereotopic ($\alpha^C\alpha^H$) and show two groups of resonances at $\sim 2.83$ ppm and $\sim 2.43$ ppm. The resonances from methine protons from ECH sequence are observed at $\sim 3.05$ ppm.

Figure 4.1. 1D $^1$H NMR spectra of polyEHC* showing a) full $^1$H NMR spectrum, b) expansion of $\alpha^C$ region of the proton spectrum.

Figure 4.2a shows the full $^{13}$C NMR spectrum of polyEHC*. The groups of resonances from $\sim 14$ ppm to $\sim 50$ppm are due to methylene and methine resonances from ethylene and 1-hexene units while the groups of resonances from $\sim 206$ppm to $\sim 216$ppm are due to various ketone carbonyl carbons. The ketone carbonyl carbon resonances are enhanced due to the $^{13}$C enrichment of those carbons. Resonances at $\sim 14$ ppm are due to the 1B$_4$ methyl groups from -C$_4$H$_9$ side chain of 1-hexene. The resonances at $\sim 23$ ppm could be assigned to the 2B$_4$ methylene groups while the two resonances at $\sim 30$ ppm and $\sim 32$ ppm are due to 3B$_4$ and 4B$_4$ methylene resonances from the butyl branch of 1-
hexene. The group of resonances at ~37.4 ppm is assigned to $\alpha^C\beta^C$ carbons from 1,4-dione structure.

Two small resonances can be seen ~44 ppm to ~49 ppm, Figure 4.2b shows the expansion of region from 44 ppm to 49 ppm; The groups of resonances at ~45.1 ppm are assigned to $\alpha^C$ methylene carbons from CHC triads while the groups of resonances at ~47.5 ppm are assigned to the methine carbons.

The ketone carbonyl from ~206 ppm to ~216 ppm show two strong groups of resonances and the expansions and be seen in Figure 4.2c. The groups of resonances at ~209 ppm is assigned to carbonyl carbons which have two $\alpha$ methylene groups while the groups of resonances at ~213 ppm is assigned to carbonyl carbons which have one $\alpha$ butyl branch.

Figure 4.2. 188.6 MHz $^{13}$C NMR spectra of polyEHC* showing a) full $^{13}$C NMR spectrum b) expansion of $\alpha^C$ methylene and $\alpha^C$ methine regions, and c) expansion of ketone carbonyl carbon region.
Quantitative NMR analysis of polyEHC*: $^1$H and $^{13}$C NMR were both used for quantitative analysis of polyEHC*. In the $^1$H NMR spectrum the three resonances between 0.7 to 1.6 ppm (region A) are from the butyl branch of 1-hexene as these resonances were found to be in a 1:5:3 ratio representing one proton from 4B$_4$: methylene (2B$_4$+3B$_4$) + (one proton from 4B$_4$): methyl (1B$_4$). Thus, this area is representative of the amount of hexene in the polymer and can be used to calculate the number of moles of 1-hexene. The amount of 1-hexene could also be calculated from the methine resonances near ~3.05 ppm, but this region suffers from a severe overlap from the methylene resonances hence the butyl branch resonances were used for the calculations. The resonances between 2.3- 3.2 ppm represents the methylene and methine protons, $\alpha$ to carbonyl carbon, from ethylene and 1-hexene. Thus, this region represents four protons from ethylene unit and three protons from the 1-hexene backbone and can be used to calculate the amount of ethylene in the polymer. The amount of carbon monoxide can also be calculated from the 2.3-3.2 ppm region (region B) as all the $\alpha^C$ resonances fall in this region and are a representative of the carbon monoxide in the polymer. As all the resonances in this region overlap with each other it is inappropriate to select one of the resonances to calculate the amount of carbon monoxide, hence, it was calculated indirectly from the fraction of 1-hexene and ethylene. Those values were used to determine the contribution of ethylene (-CH$_2$-CH$_2$-) and 1-hexene (-CH$_2$-CH-) in the region B. The equations used to calculate the mole % of each of the monomer are shown below:
\[A = k \times 9H \quad 4.1\]
\[B = k \times (4E + 3H) \quad 4.2\]

where, \(H\) is 1-hexene, \(E\) is ethylene and \(k\) is scaling factor.

Moles of ethylene and 1-hexene can be calculated by rearranging the above equations.

Therefore,
\[H = \frac{k' \times A}{9} \quad 4.3\]
\[E = \frac{k'(B - 3H)}{4} \quad 4.4\]

where, \(k' = \frac{1}{k}\).

The fraction of ethylene and 1-hexene can now be calculated from the number of moles calculated from equation 4.3 and 4.4.

Thus,
\[f_H = \frac{H}{E + H} \quad 4.5\]
\[f_E = \frac{E}{E + H} \quad 4.6\]

As discussed earlier region B can be used to calculate the amount of carbon monoxide.

Moles of carbon monoxide can now be estimated as follows using values from equation 4.5 and 4.6:

\[C = k' [f_H(B/3) + f_E(B/4)] \quad 4.7\]

where, \(f_H(B/3)\) is the contribution from the three backbone protons of 1-hexene \(\alpha\) to \(C\) and \(f_E(B/4)\) is the contribution from the four protons of ethylene \(\alpha\) to \(C\).

Total number of moles (\(S\)) can be calculated by adding the number of moles of \(E\), \(H\) and \(C\) calculated from equations 4.3, 4.4 and 4.7.

Hence,
\[S = k'[4A + 9B - 27H + 12f_HB + 9f_EB]/36 \quad 4.8\]
Thus, the mole % of each of the monomer can be calculated using appropriate values from equation 4.3, 4.4, 4.7 and 4.8:

\[
mole\% \text{ H} = \frac{[H/S]}{S} \times 100
\]

4.9

\[
mole\% \text{ E} = \frac{[E/S]}{S} \times 100
\]

4.10

\[
mole\% \text{ C} = \frac{[C/S]}{S} \times 100
\]

4.11

Table 4.1 shows the quantitative analysis of polyEHC* using $^1$H NMR.

Table 4.1 Compositional analysis of polyEHC* using $^1$H NMR.

<table>
<thead>
<tr>
<th>monomer</th>
<th>mole % polyEHC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>46</td>
</tr>
<tr>
<td>H</td>
<td>16</td>
</tr>
<tr>
<td>E</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 4.1 Compositional analysis of polyEHC* using $^1$H NMR.

$^{13}$C NMR was also used to calculate the amount of E, H and C in the polymer. The integral ratio of the four butyl branch resonances at ~14, ~23, ~30, ~32 ppm were found to be 1:1:1:1, hence they truly represent 1-hexene unit and can be used to calculate the amount of 1-hexene in the polymer. Amount of ethylene can be calculated from the resonance at ~37ppm; this resonance is representative of majority of 1-4 dione structures hence can be used to calculate ethylene. The amount of carbon monoxide in the polymer can be calculated using the resonances from regions ~37, ~45 and ~47. These regions represent $^{\alpha}C$, $^{\alpha}C^{\alpha}H$ and methine CH$_{CHC}$ from 1-hexene unit $^{\alpha}$ to C. The equations used to calculate the mole % of each of the monomers is shown below.
Regions at ~14, ~23, ~30 and ~32 ppm are proportional to the four carbon of butyl branch from 1-hexene, i.e.

\[ I_{14}+I_{23}+I_{30}+I_{32} = k \times 4H \]  

Region at ~37 ppm is proportional to two carbons from ethylene, i.e.

\[ I_{37} = k \times 2E \]  

Region at ~37, ~45 and ~47 ppm is proportional to the two units of carbon monoxide, i.e.

\[ I_{37}+I_{45}+I_{47} = k \times 2C \]  

where, \( k \) is a scaling factor, \( I \) is the integral value for the relevant region, \( E = \) ethylene, \( H = \) 1-hexene and \( C = \) carbon monoxide.

Moles of each of the monomers can be calculated by rearranging equations 4.12, 4.13, 4.14 as follows:

\[ H = k'[I_{14}+I_{23}+I_{30}+I_{32}]/4 \]  
\[ E = k'[I_{37}]/2 \]  
\[ C = k'[I_{37}+I_{45}+I_{47}]/2 \]  

where, \( k' = 1/k \).

Total number of moles can be calculated by adding the values from equation 4.15, 4.16 and 4.17.

\[ S = k'[I_{14}+I_{23}+I_{30}+I_{32}+2I_{37}+2I_{45}+2I_{47}]/4 \]  

Mole % of each of the monomers can now be calculated from the equation 4.15, 4.16, 4.17 and 4.18 as:

\[ \text{mole% } H = [H/S] \times 100 \]  
\[ \text{mole% } E = [E/S] \times 100 \]  
\[ \text{mole% } C = [C/S] \times 100 \]
The results from equations 4.19, 4.20, 4.21 are presented in Table 4.2.

Table 4.2 Compositional analysis of polyEHC* using $^{13}$C NMR.

<table>
<thead>
<tr>
<th>monomer</th>
<th>mole % polyEHC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>49</td>
</tr>
<tr>
<td>H</td>
<td>18</td>
</tr>
<tr>
<td>E</td>
<td>33</td>
</tr>
</tbody>
</table>

E = ethylene  
C = carbon monoxide  
H = 1-hexene

4.3.2 2D NMR Analysis of polyEHC*

2D gHSQC and gHMBC experiments were used for identification and confirmation of the resonances assigned using 1D NMR. More attention is paid in the assignment of the C-centered structures.

Figure 4.3 shows the gHSQC spectrum of polyEHC*. The methyl and methylene resonances due to 1-hexene and ethylene can be observed from $\delta_C = \sim 14$ ppm to $\delta_C = \sim 34$ ppm, while the resonances due to C-centered structures can be observed from $\delta_C = \sim 36$ ppm to $\delta_C = \sim 48$ ppm. Expansion of the region form $\delta_C = 36 – 48$ ppm is shown in Figure 4.4a and HMBC correlations to the ketone carbonyl carbons are shown in Figure 4.4b.

The HSQC spectrum shows a group of resonances at $\delta_C = \sim 36.5$ ppm and $\delta_H = \sim 2.63$ ppm which have been assigned to the $\alpha^C\delta^+$ methylene carbons/protons. The group of resonances due to methylene carbons/protons from CHC triads can be observed at $\delta_C = 44.23$ ppm and $\delta_H = 2.40, 2.80$ ppm, while the resonances due to methine protons/carbons
can be observed at $\delta_C = 46.75$ ppm and $\delta_H = 2.86$ ppm. These HSQC resonances show correlation in the HMBC spectrum; two groups of correlations can be observed in the ketone carbonyl region of the HMBC spectrum, the first group at $\delta_C \approx 209.06$ ppm and the second at $\delta_C \approx 212.9$ ppm. All the resonances from Figure 4.4 show correlation to these resonances in HMBC thus making the assignment almost impossible. Also, due to $^{13}$C enrichment of the ketone carbonyl carbons $^{13}$C-$^{13}$C couplings can be observed in the spectrum which makes the assignment even more difficult. Due to the poor resolution of the resonances in HMBC 3D NMR experiments were utilized for further assignment of resonances.

Figure 4.3. 2D HSQC spectrum of polyEHC*

Figure 4.4 a) Expansion of 2D HSQC showing $\alpha^C$ methylene and methine regions of polyEHC* and b) correlations of these resonances to the ketone carbonyl carbons in HMBC spectrum.
4.3.3 3D NMR Analysis of polyEHC*

As the polymer is $^{13}$C enriched at the ketone carbonyl position only C-centered structures are considered for the 3D study. Also, it is known that C does not add to C hence those structures are also not considered in the study.

Similar to polyEV*C the study the 3D HC$_A$C$_X$ and HC$_A$C$_X$-HH-TOCSY planes shown in the figures are $f_2f_3$ planes selected at $f_1$ frequency. Each $f_2f_3$ plane contains two unique $\alpha$C methylene correlations at a unique carbonyl carbon frequency ($f_i$). Each HC$_A$C$_X$ resonance is shown in bold letters ($a$, $b$, $c$, …) while the resonances due to diastereotopic protons are shown in bold letter with a prime ($a'$, $b'$, $c'$, …). The TOCSY correlations of these resonances are shown in bold letters with numerical subscripts ($a_1$, $a_2$, $a_3$, …, $a'_1$, $a'_2$, $a'_3$, …). Thus, the HC$_A$C$_X$ spectrum gives $^1$H–$^{13}$C$_\alpha$–$^{13}$CO connectivity information while HC$_A$C$_X$-HH-TOCSY correlates this fragment to the neighboring protons which share $^1$H–$^1$H couplings (i.e. correlations to the remainder of the spin system of the CXCECX where X = E or H).

Figure 4.5 shows $f_2f_3$ slices from HC$_A$C$_X$ (Figure 4.5a) and TOCSY correlation in HC$_A$C$_X$-HH-TOCSY (Figure 4.5b) from CHCEC pentad at $f_i = 212.80$ ppm (ketone carbonyl carbon, CO). The carbonyl carbon at which the slice is selected is boxed in the structure shown. As the methylene resonances $\alpha$ to carbonyl carbon and the methine resonances fall almost 10 ppm away from each other hence to improve resolution a smaller window was selected and focusing on the methine resonances and the methylene resonances bearing diastereotopic protons and the $\alpha$C methylene carbons were allowed to fold back into the spectrum. These resonances lie between the methine and methylene
resonances bearing diastereotopic protons at $\delta_C = \sim 46$ ppm after the folding. Thus, Figure 4.5a shows $H_A$-$C_A$ cross peak $b$ at $\delta_H = 2.77$ ppm, $\delta_C = 47.58$ ppm due to the methine group and another set of $H_A$-$C_A$ cross peaks $c$, $c'$ due to the methylene group on the other side of the ketone carbonyl carbon under consideration in the $HCA_C^X$ slice. Cross peak $b$ shows TOCSY correlation in Figure 4.5b to the two $\alpha^C\alpha^H$ diastereotopic protons at $b_1$ and $b'_1$ ($\delta_H = 2.32, 2.71$ ppm), further correlations were observed to the $-C_4H_9$ side chain protons at cross peak $b_2$ ($4B_4$, $\delta_H = 1.41$ ppm), $b_3$ ($3B_4$, $\delta_H = 1.13$ ppm), $b_4$ ($2B_4$, $\delta_H = 1.04$ ppm). Correlation to the $1B_4$ protons was very weak and could not be observed in the linear predicted data. No further correlations were observed to any kind of protons hence it can be concluded that the 1-hexene group has two carbonyl carbons on either sides and thus CHC part of the CHCEC structure can be confirmed. As cross peaks $c$, $c'$ due to the methylene group were also observed hence an ethylene group is present on the other side of the carbonyl carbon under consideration. These $c$, $c'$ cross peaks show only one correlation at $c_1$ ($\delta_H = 2.45$ ppm), hence it was concluded that another carbonyl carbon is present after the E unit thus confirming the CEC part of the CHCEC sequence.
Figure 4.5. $f_2f_3$ slices from 3D HC$_A$C$_X$ (a) and HC$_A$C$_X$-HH-TOCSY (b) NMR spectra showing correlations from CHCEC sequence at $f_1 = 212.98$ ppm.

Figure 4.6a and 4.6b also shows correlations from CHCEC sequence in the $f_2f_3$ slices in HC$_A$C$_X$ but at a different ketone carbonyl carbon chemical shift ($f_1 = 209.35$ ppm). The carbonyl carbon under consideration is shown boxed structure at the top of the figure. The $f_2f_3$ slices show H$_A$-C$_A$ correlation from the methylene carbon bearing diastereotopic protons (cross peaks a, a') at $\delta_H = 2.32, 2.73$ ppm, $\delta_C = 45.19$ ppm. These
protons show correlations to the neighboring methine proton at $\delta_H = 2.78$ ppm (cross peak $\mathbf{a}_1$) and also to the $-\text{C}_4\text{H}_9$ side chain at cross peak $\mathbf{a}_2$ ($4\text{B}_4$, $\delta_H = 1.41$ ppm), $\mathbf{a}_3$ ($3\text{B}_4$, $\delta_H = 1.15$ ppm), $\mathbf{a}_4$ ($2\text{B}_4$, $\delta_H = 1.04$ ppm). Here also no further correlations were observed hence it confirms the presence of CHC structure in the CHCEC pentad. The $\alpha^\text{C}\beta^\text{C}$ methylene were also observed in the HC$_\alpha$C$_\chi$ slice and are represented by $\mathbf{d}$ and $\mathbf{d}'$ and shows correlations to the one of the $\alpha^\text{C}\beta^\text{C}$ methylene protons at $\mathbf{d}'_1$ ($\delta_H = 2.67$ ppm), correlation to the other proton could not be clearly observed due to overlap from other resonances. No other correlation was observed hence it was confirmed that a ketone carbonyl carbon is present next to the ethylene thus confirming the CHCEC sequence.
Figure 4.6. \( f_2 f_3 \) slices from 3D HC\textsubscript{AX} (a) and HC\textsubscript{AX}-HH-TOCSY (b) NMR spectra showing correlations from CHCEC sequence at \( f_1 = 209.35 \) ppm.

4.4 Conclusions

Systematic study of polyEHC* again proved the utility of the 3D NMR experiments in the analysis of complex polymers. From the 2D NMR analysis of this polymer it was observed that although the \( \alpha^C \) and methine resonances were separated clearly no
conclusive assignment could be done based on the HMBC experiments as all the resonances showed correlations to the two kinds of ketone carbonyl carbon atoms. In this situation 3D experiments used previously were extremely useful as it was possible to assign resonances to pentad levels. Allowing the $\alpha^C$ methylene resonances to fold into the spectrum provided the use of smaller spectral width to increase the resolution needed for this work. From the 3D NMR studies it was concluded that C alternates with either E or H such that majority of the structures present in the polymer are of CXCXC kind where $X = E$ or H. No evidence for structure of CHCHC type where H is present head to head (Scheme 4.1, structure 3) or tail to tail (Scheme 4.1, structure 4) with respect to the central carbonyl carbon was found.
CHAPTER IV
SUMMARY

The study of a series of unlabeled poly(EVC) using various 1D and 2D NMR experiments was extremely useful to identify a variety of structures in the polymers. Although 1D NMR experiments showed overlap of resonances due to the formation of large amount of monomer environments and due to stereosequence effects, they were very useful in the identification of some unique resonances like the $\alpha$-$\beta$ unsaturated ketone resonances which were not evident in the 2D NMR spectra due to their extremely low probability of occurrence. 1D $^1$H and $^{13}$C were also used for quantitative analysis to calculate the amount of each monomer in the polymer. 2D NMR experiments, especially HSQC-TOCSY, were very useful in the assignment of various resonances at the triad level and sometimes to tetrad or pentad levels, as each resonance showed fine structure in the 2D spectra. HMBC spectra showed poor results in some cases, may be due to low probability of a particular triad or may be due to the cancellation of antiphase signals during the detection. Sample A with moderate amount of E, V and C was used as a benchmark to compare the rest of the polymers. Most of the major triads were identified using 2D NMR. Some low probability units such as VVV or CVE were also identified and confirmed using 2D NMR. The polymers also showed distinct resonances form the
chain-ends and due to short-chain branches which could be assigned. It was also concluded that the polymer does not form a variety of short-chain branches as no evidence of those structures was found in the 2D spectra. In spite of the dispersion in the 2D spectra, some of the regions (α V methylene and methine regions) showed extreme overlap of resonances. This was due to the formation of a large number of n-ads produced from monomer and stereosequence effects. It was not possible to assign resonances unambiguously in those regions. To circumvent this problem recently introduced 3D HC A C X and HC A C X-HH-TOCSY experiments were used.

A 13C enriched polymer of similar composition to sample C was used for the analysis using 3D NMR. As the overlap was observed in the α V methylene and methine regions, the polymer prepared was 13C enriched at the adjacent olefinic carbons of vinyl acetate. Initial study to identify and confirm the resonances was performed using the usual 1D and 2D NMR experiments and then the 3D NMR experiments were used to separate the overlapping resonances. During the initial setup of the 3D experiments, it was observed that only the structures from EVE triads could be detected, while resonances from EVV triads were missing. This was due to the fact that the Δ1, Δ2, τ1 and T delays in the experiment were appropriate for EVE structures. Hence, these delays were optimized such that both the structures could be observed in the 3D NMR spectra. In the EVE triad region, it was possible to identify five different pentad structures due to various environments created because of the three monomers, E, V and C, while in the m/r-EVV region; it was possible to identify two pentads for each of the m/r-EVV triads. Thus, it was possible to disperse the resonances from all these various structures and assign them at pentad levels which could not be observed in the 2D spectra.
The usefulness of the 3D NMR experiments was also shown in the study of the polyEHC\(^*\) terpolymer which was \(^{13}\)C enriched at ketone carbonyl position. The polymer was prepared with high amounts of carbon monoxide so that an alternating polymer was formed where C alternated with either E or H. The 1D analysis of the polymer using proton and carbon NMR also proved the alternating structure of the polymer. 2D NMR was not useful to identify different environments around ketone carbonyl carbons as it failed to show any resolved correlations. 3D NMR was much useful here to obtain connectivity information along the polymer chain. From the 3D NMR analysis, it was observed that the majority of the polymer structure is of CHCEC type as two different environments were identified for the ketone carbonyl carbons which showed correlations to either E or H units.

From the study of these two different terpolymers, it was found that 3D HC\(_A\)C\(_X\) and HC\(_A\)C\(_X\)-HH-TOCSY experiments can be easily used to study the structure in a polymer or any other kind of complex mixture of molecules or molecular fragments. They provide an opportunity to selectively study a part of molecules as demonstrated in the study of polyEV\(^*\)C where only V-centered structures which were one-third of the total structure were studied to resolve the overlapping structures. The identification of these structures will be useful for the better understanding of the polymerization mechanism and for the derivation of correct structure-property relationship in the polymers.
REFERENCES


55. Shell Company Homepage. [http://www.shell.com](http://www.shell.com)
APPENDIX

2D HSQC NMR spectra showing a) methyl and methylene, b) methine regions of sample A.