3D NMR Studies of C-Centered *n*-ad Structures in Poly(ethylene-*co*-*n*-butylacrylate-*co*-^{13}C-carbon monoxide) (PolyEBC*)

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ABSTRACT: Three-dimensional HC_AC_X and HC_AC_X−HH−TOCSY NMR experiments (*J. Magn. Reson*. **2004**, *168*, 352) at 750 MHz have been used to investigate the resonance assignments and monomer sequence distributions of C-centered triads and pentads in poly(ethylene-*co*-*n*-butyl acrylate-*co*-^{13}C-carbon monoxide), poly(EBC*) terpolymer prepared from ^{13}C-labeled carbon monoxide. These experiments provide spectra with correlations among mutually coupled atoms with δ_{CO} plotted along the f_1 dimension and δ_{CA} and δ_H of adjoining groups plotted along the f_2 and f_3 dimensions, respectively. The correlation among signals in three planes in a 3D NMR spectrum facilitates selective detection of the resonances from the structure fragments near the ^{13}C labeled ketone carbonyl groups. Moreover, these experiments provide enormous spectral resolution, permitting the identification of numerous unresolved signals that are overlapped in 2D ^{1}H−^{13}C HMBC NMR spectrum. The correlation of resonances involving three different nuclei (δ_H, δ_{CA}, and δ_{CO}) provides unambiguous atomic connectivity information in the polymer backbone that facilitates analysis of comonomer composition, stereo-sequence distribution and branching structures. Occasionally, these experiments provide additional proof of the methods adopted to perform chemical shift assignments from 2D HMBC NMR experiments.

Introduction

PolyEBC is generally used as a polymer modifier such as low temperature and general purpose toughenerers in ABS, and as plasticizers in PVC compounds. As high-molecular-weight flexiblizers, these resins reduce smoke and add strength and low-temperature flexibility. This combination of properties allows compounders to increase the amount of flame-retardant additives without compromising strength or flexibility and without adding liquids which increase smoke.[1] These attributes have made polyEBC valuable in applications such as single-ply roofing membranes, geomembranes, automotive interiors, pipe liners, and wire and cable insulation and jacketing.[2,3] Because of its many important uses, it is desirable to completely assign the NMR resonances of polyEBC in order to facilitate identification of unique structures present in this terpolymer and to determine structure−property relationships.

Complete NMR resonance assignments for terpolymers (polymers with three different comonomer units) are usually complicated by overlapping resonances from the numerous triads, pentads, and higher *n*-ads that arise from the permutation of more than two different monomer units in a comonomer sequence. The arrangement of different monomer units in a comonomer sequence along with branching structures and stereo regularity along the polymer backbone makes the NMR spectrum very complex, preventing the unambiguous assignments of individual resonances.[4] In terpolymers, the presence of three different monomers warrants pentad level compositional assignment for complete characterization and meaningful correlations of structure−property relationships.

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One-dimensional NMR spectroscopy, in particular, ^{1}H and ^{13}C NMR has been widely used to investigate polymer structure, particularly for identifying monomer and stereo-sequence distributions in homo and copolymers.[5] ^{13}C NMR is particularly useful because of its wide chemical shift distributions (more than 250 ppm), narrow resonance lines (^{1}H decoupled spectrum) and finally the intensity of the unambiguously identified resonances can provide quantitative compositional information for polymers.[6] However, spectral complexity from overlapping resonances in the case of terpolymers is still a profound problem due to the numerous unique structural environments arising from complex arrangements of the three comonomer units, due to different reactivity ratios and stereochemistry, as well as intramolecular rearrangements. Over the past two decades, 2D correlation NMR methods such as ^{1}H−^{13}C heteronuclear multiple-quantum coherence (HMQC), heteronuclear single-quantum coherence (HSQC) and heteronuclear multiple-bond coherence (HMBC) NMR experiments have become effective for investigating the microstructures of homo- and copolymers by dispersing overlapping resonances into multiple dimensions.[7,8] Although single and multiple bond correlated 2D NMR spectra provide sufficient resolution for the assignment of various copolymers,[9,10] it has usually failed to provide sufficient dispersion to resolve the overlapping resonances in the spectra of complex terpolymers.

The permutations of triads for this polymer are listed in Table 1. If polymerization is assumed to occur solely in a head-to-tail manner, up to 27 unique triad monomer sequences are possible.[11] Additionally, some of the triad monomer sequences have two or more stereosequences, since B units form stereogenic centers in the polymer backbone and two adjoining B units give rise to *m* and *r* dyad structures. Although there are 33 nonidentical structural permutations, some of these triads

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Table 1. Possible Triad Sequences for Poly(EBC)[a]

E-center	B-center	C-center
EEE	BBB(3)	CCC
EEB	EBB(2)	ECC
BEB(2)	EBE	ECE
CEE	CBB(2)/BBC(2)	BCC/CCB
CEC	CBC	BCB(2)
BEC/CEB	EBC/CBE	ECB/BCE

[a] E = ethylene, B = *n*-butyl acrylate, and C = carbon monoxide. The numbers in parentheses indicate the number of triad stereosequences when more than one is possible.

are not likely for various reasons such as low reaction probability due to concentration, steric and electronic effects. The complexity of the mixture is further increased because of the formation of additional structures from backbiting reactions and chain-end structures.[12] The enormous variety of structures in the mixture produces numerous overlapping peaks even in the 2D-NMR spectra even at 750 MHz. Since the structures in this mixture are part of the same polymer chain, separation and analysis of individual components is not an option.

Wyzgoski et al.[13] studied unlabeled polyEBC, in attempts to solve the complex problem of assigning the resonances of the terpolymer with the help of 1D NMR, DEPT, HMQC, HSQC, and HMBC 2D-NMR spectra. They were only partially successful at assigning resonances arising from a number of triad structures and were able to detect some of the cross-peaks consistent with the presence of branching and chain-end structures. Monwar et al.[14] used ^{1}H-detected ^{1}H−^{13}C correlated 2D NMR of poly(ethylene-*co*-2-^{13}C-*n*-butyl acrylate-*co*-carbon monoxide) obtained from 2-^{13}C-*n*-butyl acrylate (polyEB*^{2}C) and poly(ethylene-*co*-1-^{13}C-*n*-butyl acrylate-*co*-carbon monoxide) obtained from 1-^{13}C-*n*-butyl acrylate (polyEB*^{1}C) to selectively detect and assign the resonances of B-centered pentads in poly(EBC). By using the selective enhancement and spectral simplification provided by selective labeling, they were successful in confirming the prior assignments made from NMR studies of unlabeled polymer, and were able to detect some new resonances from species present in low concentration. Using a similar strategy, Al-Amri et al.[15] used ^{1}H−^{13}C HMBC 2D NMR to detect and assign the resonances of C-centered pentads in poly(ethylene-*co*-*n*-butyl acrylate-*co*-^{13}C-carbon monoxide) obtained from ^{13}C-carbon monoxide (polyEBC*). These studies showed the advantage of selective ^{13}C-labeling along with 2D NMR measurements at very high field which permit the characterization of extremely complex mixtures of polymer structures at the pentad level, even for pentads that are far less than 1% of the sequences. However, these 2D-NMR studies were unable to provide a complete set of resonance assignments for this complex terpolymer.

Of late, HXY (X = ^{13}C, Y = ^{15}N, ^{19}F, ^{29}Si, ^{31}P, ^{119}Sn) 3D NMR methods have been used to overcome the peak overlap problem by introducing a third frequency dimension and dispersing the overlapped peaks into a number of 2D planes in the 3D NMR spectra of complex polymeric systems.[16,17] Unfortunately, most of the synthetic polymers of research and commercial significance are hydrocarbon based and lack a suitable third NMR active nucleus (Y); hence HXY 3D-NMR methods are not suitable in systems such as poly(EBC).

Recently a suite of 3D NMR experiments (HC_AC_X, HC_AC_X−HH−TOCSY and HC_AC_X−CC−TOCSY) was described which enables the assignment of resonances from backbone atoms in ^{13}C labeled hydrocarbon-based polymers.[18,19] These experiments offer a powerful alternative to the more conventional approach which relies on sequential assignments of polymers via 1D and 2D NMR experiments. The versatility of the triple-resonance 3D-NMR approach has been demonstrated using a sample of poly(ethylene-*co*-*n*-butyl acrylate-*co*-carbon monoxide) poly-(EB*C) prepared from 1-^{13}C-*n*-butyl acrylate (CH_2═CH−$^{13}CO_2$-*n*-C_4H_9) to assign the resonances of B-centered *n*-ads.[20] In this paper we report the application of this suite of 3D-NMR experiments to study the structures of C-centered *n*-ads in poly-(ethylene-*co*-*n*-butyl acrylate-*co*-^{13}C-carbon monoxide) from ^{13}C-labeled carbon monoxide poly(EBC*) in order to study the microstructure of this complex terpolymer.

Experimental Section

Preparation of Poly(EBC*) for NMR Analysis. The preparation and 2D NMR characterization of the poly(EBC*) sample has been previously described.[15] The polymer's composition is (61:32:7) mole % E:B:C (ethylene:*n*-butyl acrylate:carbon monoxide) based on 1D ^{1}H NMR data. To prepare solutions for NMR studies, crystals of 1,4-dichlorobenzene-d_4 were melted and 20.0 mg of the polymer was dissolved in 0.7 mL melt to produce 3% (w/v) polymer solutions. The samples were heated to 120 °C and rotated at 20 rpm in a Kugelrohr oven for 6 h to obtain a uniform dispersion of the polymer in solution and to minimize the formation of air bubbles. Hexamethyldisiloxane (HMDS) was added as an internal chemical shift standard (δ_H = 0.09 ppm; δ_C = 2.0 ppm). All NMR spectra were collected at 120 °C on a Varian INOVA 750 MHz NMR spectrometer equipped with four RF channels, a Performa-II pulsed field gradient accessory, and Varian's Protein Pack software module. For comparison purpose, ^{13}C NMR data from an unlabeled polymer sample poly(EBC) with E:B:C composition of 85:12:3 was used.[13]

3D HC_AC_X and HC_AC_X═HH═TOCSY NMR of Poly-(EBC*). 3D HC_AC_X and HC_AC_X−HH−TOCSY NMR spectra were collected with a Nalorac ^{1}H/^{13}C/^{15}N 5 mm probe and *z*-axis pulse field gradient (PFG) accessory, operating at 120 °C. The details of the pulse sequence and parameter optimization procedure have been previously described.[19] The 3D HC_AC_X NMR pulse sequence was used to correlate H_A (2.0−3.0 ppm) proton resonances in f_3, the $^{13}C_A$ carbon resonances (39.0−46.0 ppm) in f_2, and the $^{13}C_{CO}$ (205.0−209.0 ppm) carbonyl resonances in f_1. Spectral windows in the f_1 ($^{13}C_{CO}$), f_2 ($^{13}C_A$), and f_3 (^{1}H) dimensions were 1506, 3400, and 6746 Hz, respectively. ^{1}H, $^{13}C_A$, and $^{13}C_X$ offsets were set at f_3 = 3.55, f_2 = 39.0, and f_1 = 208.0 ppm, respectively. The spectra were collected with $\pi/2$ pulse widths of 10.3 and 16.0 μs in the ^{1}H and ^{13}C channels, respectively. The width of the selective square pulses to $^{13}C_A$ or $^{13}C_X$ was set based on the difference in the frequency offsets between the two regions, such that selective $^{13}C_A$ pulse did not excite $^{13}C_X$ nuclei, and vice versa. The selective $\pi/2$ and π pulse widths on either $^{13}C_A$ or ^{13}Cx were 30.4 and 27.0 μs respectively based on the offset of 31867 Hz between the $^{13}C_A$ and $^{13}C_X$ regions. The selective π pulse to $^{13}C_A$ in middle of the $^{13}C_X$ (t_1) evolution period was a shifted laminar pulse[21] to invert $^{13}C_A$ resonances. Gradient pulses g_1-g_9 along the *z*-axis were applied with amplitudes and durations: g_1 = 0.3 T/m, 1.0 ms; g_2 = 0.15 T/m, 0.75 ms; g_3 = 0.3 T/m, 1.0 ms; g_4 = 0.2 T/m, 0.3 ms; g_5 = 0.15 T/m, 0.2 ms; g_6 = −/+ 0.25 T/m, 1.6 ms; g_7 = 0.15 T/m,1.0 ms; g_8 = 0.25 T/m, 0.8 ms; and g_9 = 0.25 T/m, 0.4 ms. The z-gradient pulses g_6 and g_9 were used for ^{1}H−^{13}C coherence selection with area ratio of 4:1. WALTZ-16 decoupling with 7.5 kHz field strength was employed during delays τ_1, t_1, and T, to remove the ^{1}H couplings in the indirectly detected dimensions. Quadrature detection in the f_1 ($^{13}C_X$) dimension was achieved by alternating the phase of φ_1 in a States-TPPI manner.[22] Echo/antiecho selection in the f_2 ($^{13}C_A$) dimension was achieved by inverting the amplitude of the g_6 gradient pulse and the phase φ_4.[23] Axial peak displacement in the f_2 dimension was obtained by inverting the phase of φ_2 and the receiver (φ_r) on every second increment. For the spectra from both sequences, the delays were as follows: 1.0 s recycle delay, 0.15 s acquisition time, constant evolution delay $2T$ = 10.0 ms; Δ = 1.8 ms; τ_b = 2.1 ms; and τ_c = 1.5 ms. The spectra were collected with 2048 time domain data points with 17.0 kHz GARP ^{13}C-decoupling;

Table 2. Possible Pentad Sequences along with Probability of Their Occurrence in Poly(EBC*)[a]

ECE	% probability	ECB	% probability
EECEE	0.97	**EECBE**	0.51
EECEB	0.51	**EECBB(2)**	0.27
EECEC	0.11	EECBC	0.06
BECEE	0.51	**BECBE(2)**	0.27
BECEB	0.27	**BECBB(4)**	0.14
BECEC	0.06	BECBC(2)	0.03
CECEE	0.11	CECBE	0.06
CECEB	0.06	CECBB(2)	0.03
CECEC	0.01	CECBC	0.01
ECE	**2.61**	**ECB**	**1.38**

[a] Assumes E:B:C ratio of 61:32:7 determined for poly(EBC*).

32 transients were averaged for each of 2 × 24 and 2 × 32 FID's in the f_1 and f_2 dimensions, respectively.

The 3D NMR data were processed using Varian's VNMR software with *f1coef* = '1 0 0 0 0 0−1 0' and *f2coef* = '1 0−1 0 0−1 0−1'. The time domain data were forward linear predicted to four times the original number of data points in both the f_1 and f_2 dimensions, zero filled to 512 × 512 × 4096 data points and weighted with a shifted sin bell function before Fourier transformation.

In 3D HC_AC_X−HH−TOCSY NMR experiment, spin-locking in ^1H (f_3) dimension was achieved by applying a DIPSI-2 isotropic mixing sequence for 30.0 ms with 9.0 kHz field strength which effects proton magnetization transfer encompassing up to four bonds in the spin system. Other parameters of the pulse sequence remain the same as in the HC_AC_X experiment described above.

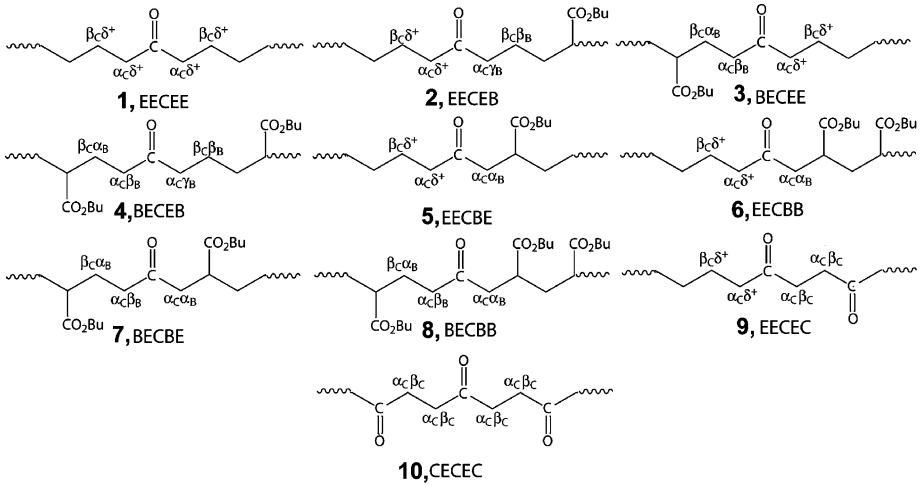
Results and Discussion

Structures and Nomenclature. The possible triad monomer sequences are shown in Table 1 and can be categorized into three subgroups depending on the central monomer unit. In this paper, the focus is on the assignment of structures (monomer sequences and branching structures from backbiting reactions) near the ^{13}C labeled carbon monoxide (C-centered triads and pentads). If stereosequence effects are ignored there are total of 243 permutations of pentad sequences in this terpolymer. Although a total of only 9 C-centered triads are possible as shown in Table 1, the presence of some of triads (ca. CCC, ECC, CCB/BCC, and BCB) are not considered during the interpretation of the spectra due to the very low probability of addition of C units to another C units in the chain.[24] Prior work has also shown that the probability of C adding to B unit is low, and thus resonances from BC dyads are only detected from long-term signal averaging of spectra from doubly ^{13}C labeled polymer.[25] The probabilities of occurrence—based on composition alone and not including the reactivity ratios of the monomers—of particular C-centered pentads in poly(EBC*) are listed in Table 2. True probabilities will be somewhat different due to the differing reactivity ratios of the various monomers, but these data serve as a rough guide for estimating the intensities of the NMR signals.

In describing the structures and their resonance assignments, the nomenclature of labeling the atoms proposed by Wyzgoski et al.[13] has been followed. Since the spectra from the terpolymer samples contain resonances characteristic of long sequences of ethylene monomer units, the nomenclature is based on that used to label the atoms in general structure for polyethylene. This is based on the polyethylene nomenclature first defined by Carman[26] and modified by Dorman[27] and Randall[5] and exemplified in a high field NMR study by Liu et al.[28] Methylene carbons along the backbone are identified by a pair of Greek letters to indicate the distances to the branches in either direction. Carbons in the side chains are designated by iB_n where "i" indicates the position in the branch starting with the methyl in position 1, and the subscript "*n*" denotes the length of the branch.

The terpolymer samples also contain branching structures resulting from the addition reactions of carbon monoxide and *n*-butyl acrylate. The pentads relevant to the work described in this paper are represented by **1**−**10** in Scheme 1. The same basic nomenclature used for ethylene/α-olefin copolymers has been adapted as follows: a superscript B or C is used to designate a branch formed by insertion of a B or C monomer unit in the polymer chain. Here, the in-chain carbonyl formed by insertion of carbon monoxide is defined as a branch in which two methylene protons are replaced with a double bond to oxygen. In defining the structures and resonance assignments for each C-centered pentad, the structures of two triads composed of the central C-unit and the two comonomer units to its left and right along the polymer chain must be considered. An example of the nomenclature system for these relevant structures resulting from incorporation of C monomer units into the polyethylene chain is shown (**1**) in Scheme 1. In this structure of an EE**C**EE pentad, the CEE triad fragments contain methylene carbons α and β to a ketone carbonyl group that are designated as $\alpha^C\delta^+$ and $\beta^C\delta^+$ respectively. The 1,4-diones (**9** and **10**) in Scheme 1, contain equivalent methylene units that are designated $\alpha^C\beta^C$, since these carbons are both α and β to branches formed from carbon monoxide. Scheme 1 shows pentad structures relevant to this work, with corresponding labels illustrating the nomen-

Scheme 1. Structures and Nomenclature for Relevant C-Centered Pentads (1-10) from Poly(ethylene-*co*-*n*-butyl acrylate-*co*-carbon monoxide)



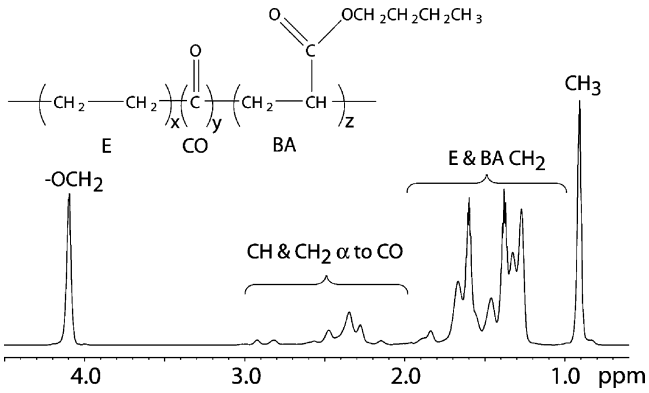


Figure 1. 750 MHz ^{1}H NMR spectrum of poly(EBC*).

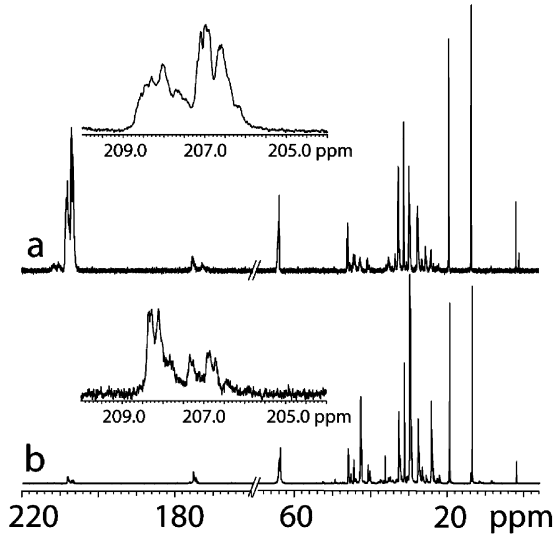


Figure 2. 188.6 MHz ^{13}C NMR spectra of poly(ethylene-*co*-*n*-butyl acrylate-*co*-carbon monoxide) (a) labeled poly(EBC*) (E:B:C = 61:32:7) and (b) unlabeled poly(EBC) (E:B:C = 85:12:3) (expanded region shows ketone carbonyl region of the each spectrum).

clature for describing their carbon atoms. Because C-units contribute only one carbon to the polymer backbone, the monomer sequence order is relevant; e.g., ECB and BCE triads are not identical structures. In this paper, the unlabeled polymer is given the acronym poly(EBC), while the ^{13}C-labeled polymers (from ^{13}C labeled carbon monoxide) is designated by poly(EBC*).

The 1D ^{1}H NMR spectrum of poly(EBC*) is shown in Figure 1. The peaks are broad and overlapped in aliphatic region (1.0−3.0 ppm) of the spectrum to an extent that it is difficult to unambiguously assign resonances from methine and methylene protons neighboring to ^{13}C═O in C-centered *n*-ads (2.0−3.0 ppm). Although the quantitative^{1}H NMR spectrum can be used to determine mole % composition, it has very little utility for determining the microstructure in this terpolymer. The 1D ^{13}C NMR spectrum of poly(EBC*) terpolymer selectively labeled in the ketone-carbonyl carbon positions is shown in Figure 2a along with the spectrum of the unlabeled polymer poly(EBC) (having composition E:B:C = 85:12:3) in Figure 2b. The spectrum from the ^{13}C-labeled polymer shows the expected enhancements of peaks from ^{13}C-labeling in the 205.0−209.0 ppm region. Additionally, numerous weak peaks, that are not clearly visible in the unlabeled polymer spectrum, appear in this region. At the same time, some peaks in the aliphatic region from (10.0−65.0 ppm) which are seen in the spectrum of the unlabeled polymer are not observed, as a sample of lower concentration was used to produce the spectrum of poly(EBC*),

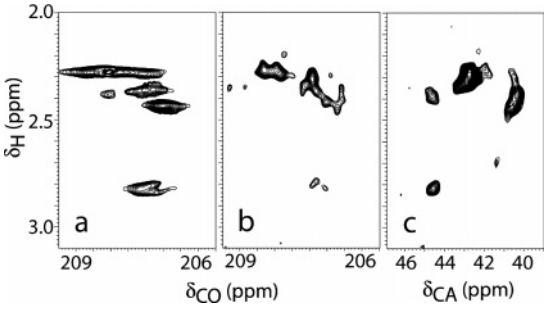


Figure 3. 2D NMR spectra of poly(EBC*) showing ^{1}H−^{13}C correlations: (a) 2D HMBC NMR spectrum showing correlations between the H_A and C_{CO}; (b) f_1f_3 planes from truncated 3D HC_AC_X spectrum showing correlations between H_A and C_{CO}; (c) f_2f_3 planes from truncated 3D HC_AC_X spectrum showing correlations between H_A and C_{CA}.

and ^{13}C−^{13}C homonuclear couplings reduce some of the peak intensities. The use of a lower concentration sample increases molecular mobility (to compensate for reduced mobility caused by higher branching), decreases the peak line widths, and improves the quality of *n*D-NMR spectra, which rely on the ability to resolve many small couplings to produce cross-peaks.

Expansions of the ketone-carbonyl region from the ^{13}C NMR spectra of labeled poly(EBC*) and unlabeled poly(EBC) are shown as inserts in Figure 2. Many intense peaks from selective ^{13}C-labeling are detected between 205 and 209.0 ppm in the spectrum of the labeled polymer. These ^{13}C peaks have broad resonance patterns due to many overlapping structures. Another notable feature in the expanded carbonyl region is the intensity variation between 206 and 207.5 and 207.5−209.0 ppm resonances in labeled and unlabeled polymers. This variation is due to the lower B content in the unlabeled polymer (E:B:C = 85:12:3) compared to the labeled polymer sample (E:B:C* = 61:32:7). The peaks in the 206.0−207.5 ppm region are enhanced in the spectrum of the ^{13}C labeled polymer (inset in Figure 2a) relative to the peaks in the same region of the spectrum from unlabeled polymer (insert in Figure 2b). The differences in the spectrum are a result of deliberately synthesizing labeled polymer with higher than usual B content (32 mol % compared to 12 mol %) to facilitate the detection and assignment of resonances from C-centered *n*-ads containing B units, which normally have very low occurrence. The signal-to-noise ratio in the ketone carbonyl region of the ^{13}C NMR spectrum of the labeled polymer is higher as expected from the ca. 100-fold increase in the amount of the ^{13}C in the labeled ketone carbonyl carbons. More than two dozen overlapping peaks arising from ketone carbonyl carbons present in different *n*-ad environments are observed that are not possible to assign completely from the 1D NMR spectra alone.

2D NMR. Figure 3a shows the 2D HMBC NMR spectrum of the ketone carbonyl region (205.0−210.0 ppm) of poly(EBC*) sample. This spectrum shows the correlations among the ketone carbonyl carbons (δ_{CO}) and α^C and β^C protons in ECE and ECB triads based on $^2J_{CH}$ and $^3J_{CH}$ couplings. As discussed above, the presence of XCC triad sequences (X is E, B, or C) in the polymer chain are not considered for assignment purposes. The HMBC spectrum shows a number of correlations that are sensitive to structure variations at least two monomers units away in a pentad sequence. This spectrum provides atomic connectivity information and unambiguous assignments for a number of resonances. However, it shows significant overlap in the 2.2−2.5 ppm region in the proton (f_2) dimension of the HMBC spectrum of poly(EBC*). This is due to the minor difference in the chemical shift of the carbonyl carbon resonance based on both adjacent monomer units on either side of the C

unit i.e., triads. There will be still smaller differences between the chemical shifts from variations in comonomer units in pentad structures. Similar overlap is also observed for the cross-peaks in 2.80−2.85 ppm region.

Figure 3b shows the f_1f_3 ($^1H-^{13}C_{CO}$) plane from the truncated 3D HC_AC_X NMR spectrum of poly(EBC*). The 3D HC_AC_X NMR experiment disperses $^1H-^{13}C_A$ correlations into a third dimension based on the chemical shifts of the $^{13}C_X$ to which they are directly attached. The spectrum in Figure 3b shows the same $^1H-^{13}C_A$-$^{13}C_{CO}$ 2-bond ($^2J_{CH}$) correlations observed in the HMBC spectrum, without interferences from 3-bond correlations. This makes the spectrum in Figure 3b much simpler compared to the corresponding region of the 2D HMBC spectrum (Figure 3a). It is possible to clearly identify 10 cross-peaks in this spectrum due to different WXCYZ pentads. By comparison, some of the cross-peaks in the HMBC spectrum are missing in the truncated 3D spectrum; these missing peaks may be from three-bond $^1H-^{13}C$ correlations and structural units with very low probability (Table 2). It may be that losses due to relaxation are more severe in the HMBC experiment, which relies on long delays required by small two- and three-bond couplings, whereas the 3D experiment uses much shorter delays based on the larger one-bond $^1J_{CH}$ and $^1J_{CC}$ couplings. The f_2f_3 ($^1H-^{13}C_A$) plane from the truncated 3D HC_AC_X NMR spectrum is shown in Figure 3c. This spectrum contains one bond $^1H-^{13}C_A-^{13}C_X$ correlations much like the HMQC spectrum. In this truncated 3D HC_AC_X NMR spectrum, only the correlations between resonances of protons and carbons of CH_n groups that directly bound (α) to ^{13}CO are detected, in comparison to the HMQC and HSQC spectra which show $^1H-^{13}C$ cross-peaks for all the CH_n groups in the molecule. Thus, an edited $^1H-^{13}C_A-^{13}C_X$ spectrum of the C-centered units is obtained from the 3D pulse sequence.

3D NMR. Analysis of 3D Data and Resonance Assignments. Among all of the possible triad sequences listed in Table 1, only the C-centered *n*-ad sequences listed in the last column can be observed in the 3D HC_AC_X spectrum. Other correlations from E- and B-centered structures are filtered from the spectrum by selective excitation of the H_A, C_A and CO (ketone carbonyl) resonances of the C-centered units. Among the many pentad structures possible, only structures with higher probability of occurrence are considered for assignments, e.g., EE**C**EE, EE**C**EB, EBCEE, BE**C**EE, BE**C**EB, EE**C**BE, EE**C**BB, BE**C**BE, BE**C**BB, and EE**C**EC; other sequences are present in concentrations that are below the detection limit of the experiment. In assigning the cross-peaks in the 3D NMR spectrum, it has been considered that proton shifts show sensitivity to triad monomer sequences while carbonyl carbon shifts are sensitive to pentad sequences. Assignments of the cross-peaks are made depending on the unique chemical shift of the carbonyl carbon (δ_{CO}), Planes at the shift of each ketone carbonyl group show f_2f_3 correlations, i.e., H_A and C_A correlations for the two groups, one on each side of the carbonyl. Although chemical shifts of many H_A-C_A cross-peaks are very similar in pentad sequences, unique H_A and C_A cross-peaks are determined by looking through f_1f_3 planes (H_A and C_{CO} cross-peaks) that show a number of different carbonyl shifts corresponding to particular C_A planes.

In analyzing the planes and assigning the resonances the following nomenclature has been used. Each f_2f_3 plane from the 3D HC_AC_X and HC_AC_X−HH−TOCSY is designated with letter (a, b, c, etc.) corresponding to a particular carbonyl shift (δ_{CO}). Unlike our previous work, in this study, each f_2f_3 plane shows more than one cross-peak depending on the number of unique H_A proton shifts on either side of the carbonyl carbon. The cross-peaks in the f_2f_3 planes of 3D HC_AC_X NMR experiment are designated with the letter of the plane (a, b, c, etc.) along with a subscript 1, 2, 3, etc. to identify correlations of the two different CH_n groups attached to either side of the carbonyl carbon. The cross-peaks from the carbons on the left of the carbonyl carbon (i.e., from the monomer unit to which the carbon monoxide adds during the polymerization) are numbered with odd integer subscript values while carbons that are right are numbered with even integer subscript values. For example, if the α^C carbon on left side of the center carbonyl carbon is numbered a_1, then the carbon next to it, i.e., the β^C carbon, is numbered as a_3 and so on. The sensitivity of the 3D HC_AC_X experiment with this sample poly(EBC*) is less compared to *n*-butyl acrylate labeled polymer poly(EB*C)[20] due to magnetization transfer from the singly labeled carbonyl carbon to two unlabeled carbons, followed by transfer to four protons of α methylene groups. This resulted in cross-peaks with lower signal-to-noise especially for low occurrence structures. However, this problem is more evident in the 3D HC_AC_X−HH−TOCSY experiment as the H_A proton magnetization is transferred to all the protons in the two spin system on either side of the carbonyl carbon, further reducing the cross-peak intensities for various structures in pentad sequences. With a 30 ms mixing time in the 3D HC_AC_X−HH−TOCSY experiment, only correlations from β protons are observed. We have failed to observe correlations to γ protons in most of the cases. There is no improvement in the efficiency of magnetization transfer to the β protons, even after increasing the TOCSY mixing time to 80 ms. At large mixing times, the 3D HC_AC_X−HH−TOCSY spectrum is too noisy to allow reliable peak identification.

The resonances of H_A protons are sensitive to changes in the structures of the triad monomer sequences on ether side of the C-centered pentad sequence. The spectra are far too complex to be due to only pentad monomer sequences with the basic triad sequences (ECE, BCE, ECB, and BCB) possible, and sensitivity to heptad monomer sequences would lead to spectra that are much more complex than those obtained here. One logical and systematic way to approach interpreting the 3D HC_AC_X and HC_AC_X−HH−TOCSY spectra is to recognize that each ketone carbonyl carbon exists in a C-centered pentad−WX**C**YZ (where W and Z represent E, C or B units and X and Y are E or B units). The pentad will contain HC_AC_X correlations to α^C protons of X and Y monomer units in WX**C** and **C**YZ triads. The HC_AC_X−HH−TOCSY spectrum will exhibit correlations to α^C and β^C protons of X and Y monomer units in WX**C** and **C**YZ triads.[18] The shifts of protons in monomers X and Y yield distinctive patterns depending upon W and Z, respectively.[25] Different ^1H patterns can be resolved at each CO shift, and then it becomes a trivial matter to identify two triad components on either side of the CO group in each pentad sequences. Unlike 2D HMBC, it is far less likely to produce patterns from overlapping C−H correlation so it is much easier to recognize these patterns and to identify the WX**C**YZ pentads. For example, the f_2f_3 plane at the ^{13}C carbonyl shift of the center carbonyl carbon in a BE**C**EE pentad will exhibit correlations to two sets of ethylene α^C and β^C proton resonances from the B*E***C** and **C***E*E triads on either side of the central **C** in the pentad unit. Each of these triads will yield a unique ^1H chemical shift pattern as one E is attached to B and C units while the other E is attached to C and E units. In addition, protons of the CH_2 group α to a B unit shows two distinct ^1H chemical shifts due to the diastereotopic nature of two geminal protons. Interpretation of the 3D-NMR spectrum is simply a matter of recognizing

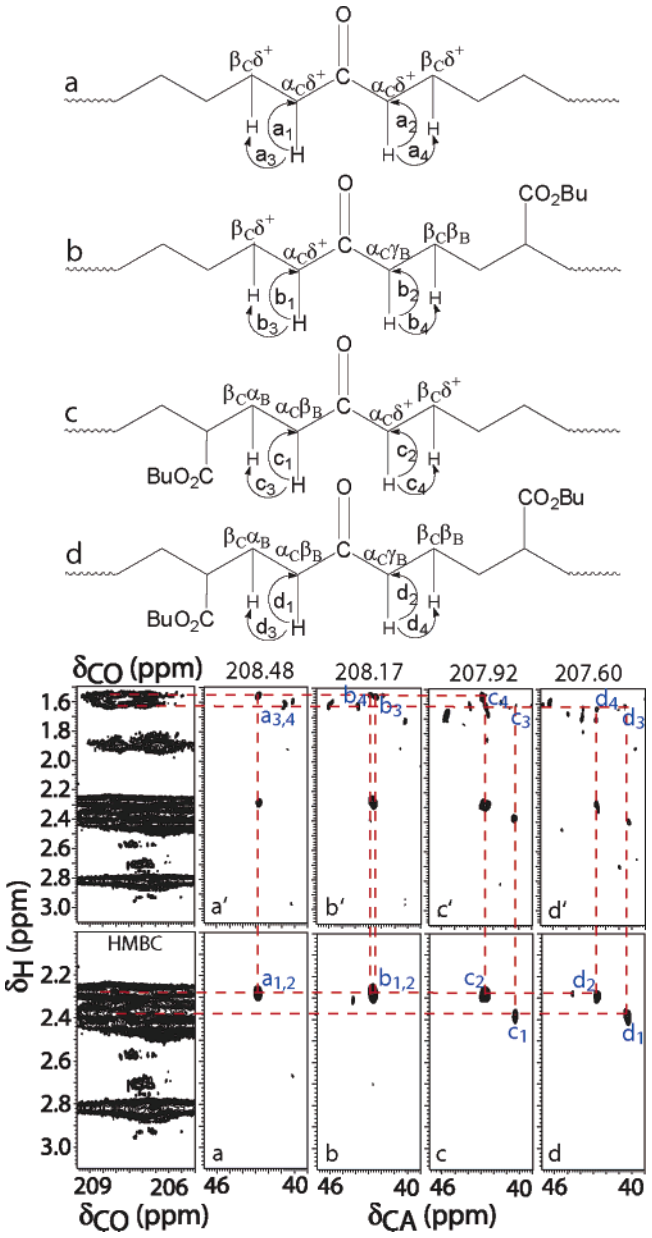


Figure 4. Slices from 2D $^{1}H-^{13}C$ HMBC (upper and lower left) and f_2f_3 planes of 3D HC_AC_X (a−d) and HC_AC_X−HH−TOCSY (a′−d′) NMR spectra along with structures corresponding to individual pentad sequences: (a and a′) EECEE; (b and b′) EECEB; (c and c′) BECEE; (d and d′) BECEB.

the two patterns at each of the ^{13}C chemical shifts. For symmetric pentads such as EE**C**EE, equivalent patterns will be superimposed from the E*E***C** and **C***E*E triads on either side of the central **C**-unit. The downfield resonances at δ_H from 2.2 to 3.1 ppm have chemical shifts corresponding to protons α to carbonyl groups. In every sequence except CEC, protons α to carbonyl group (α^C) have different chemical shifts compared to the protons β to the carbonyl groups (β^C). However, in CEC sequences all four methylene protons $\alpha^C\beta^C$ are approximately equivalent. Therefore, the proton resonances near 2.57 ppm are attributed to the methylene groups in CEC triads.

WECEZ Pentads. Figure 4 shows f_2f_3 planes corresponding to WE**C**EZ pentad sequences from 3D HC_AC_X (bottom, a−d) and HC_AC_X−HH−TOCSY (top, a′−d′) NMR spectra along with the corresponding regions of the HMBC NMR spectrum of poly(EBC*). Pentad structure fragments are presented at the top of the figure showing correlations that are observed in the 3D NMR spectra. A total of four different sets of f_2f_3 planes are displayed corresponding to the four different carbonyl shifts listed on top of each set of slices. The chemical shifts of identified cross-peaks are given in Table 3. In plane a (f_1 (δ_{CO}) = 208.48 ppm), one cross-peak, $a_{1,2}$ at δ_H = 2.29 ppm and δ_C = 42.89 ppm is assigned to symmetrical EE**C**EE pentads. Only one cross-peak in this plane (Figure 4a) indicates both $^{1}H_A-^{13}C_A$ correlations from the $\alpha^C\delta^+$ methylenes on either side of the carbonyl group (i.e., a_1 and a_2) have the same chemical shift. This is due to the chemical equivalence of methylene groups (i.e., $\alpha^C\delta^+$ in both EEC and CEE triads) in EE**C**EE pentad sequences. In the corresponding plane from the HC_AC_X−HH−TOCSY spectrum (Figure 4a′), in addition to cross-peak, $a_{1,2}$, there is another cross-peak, $a_{3,4}$ (representing both a_3 and a_4) which appears at δ_H = 1.56 ppm. This cross-peak ($a_{3,4}$) is assigned to equivalent $\beta^C\delta^+$ methylene groups of ethylene units on either side of the carbonyl carbon in EE**C**EE pentads. Both of these cross-peaks are observed in the HMBC spectrum of the poly(EBC*), however, due to severe overlap the exact peak location is not obvious from the 2D spectrum. Although we chose the 3D plane with the highest cross-peak intensity to show the presence of the EE**C**EE pentad, it is obvious from the analysis of the 3D data that more unique structures could be resolved. The variation of the environment around the pentads in higher *n*-ads accounts for the different ^{13}C chemical shifts of the cross-peaks, but these higher *n*-ads cannot be assigned from the available data. The degree of spectral simplification in going from the 2D to the 3D spectrum is astounding. This makes the shift assignment unambiguous.

Figure 4b and b′ shows selected regions from the f_2f_3 planes of HC_AC_X and HC_AC_X−HH−TOCSY spectra at f_1 = 208.17 ppm. In f_2f_3 planes from HC_AC_X spectrum (Figure 4b), one cross-peak, $b_{1,2}$ (representing b_1 and b_2) is identified at δ_H = 2.27 ppm and δ_C = 42.70 ppm. Although the δ_H position of this cross-peak is similar to that of $a_{1,2}$, there is a difference in the δ_{CA} position. Moreover, this f_1f_3 plane is resolved from the former in the ^{13}C carbonyl chemical shift dimension (Supplemental Figure 3 in the Supporting Information) confirming the assignment of this peak to a unique pentad sequence. However, if this cross-peak is not from symmetrical EE**C**EE pentad sequence, then it should show two unique cross-peaks with any change of W and/or Z units on either side WE**C**EZ pentad

Table 3. NMR Resonance Assignments of ECE-centered Pentads from 3D NMR Data for Poly(EBC*)

type of carbonyl carbon	pentad sequence	carbonyl carbon shift (ppm)	1		3		2		4	
			δ_C (ppm)	δ_H (ppm)	δ_C (ppm)	δ_H (ppm)	δ_C (ppm)	δ_H (ppm)	δ_C (ppm)	δ_H (ppm)
a	EECEE	208.48	42.89	2.29	42.88	1.55	42.89	2.29	42.88	1.55
b	EECEB	208.17	42.73	2.28	42.44	1.56	42.73	2.28	42.88	1.54
c	BECEE	207.92	40.36	2.39	40.36	1.64	42.66	2.28	42.66	1.55
d	BECEB	207.60	40.37	2.38	40.37	1.64	42.75	2.29	42.75	1.65
e	EECBE	206.98	43.10	2.32	43.10	1.60	44.58	2.38/2.82	44.58	2.94
f	EECBB	206.90	42.98	2.33	42.98	1.60	44.50	2.39/2.83	44.50	2.93
g	BECBE	206.48	40.74	2.43	40.74	1.90	44.64	2.41/2.83	44.64	2.94
h	BECBB	206.23	40.62	2.44	40.62	1.90	44.33	2.47	–	–

sequence. In addition, corresponding TOCSY correlations in Figure 4b′ shows two cross-peaks b_3 and b_4 at $\delta_H = 1.55$, $\delta_C = 42.82$ and $\delta_H = 1.54$, $\delta_C = 42.48$ ppm, respectively. The shift of b_3 is the same as that of $a_{3,4}$, which is assigned above to $\beta^C\delta^+$ carbons of EEC triad in EE**C**EX pentad. Moreover the shift of b_4 peak is slightly different (δ_C shift upfield by ~0.4 ppm) compared to that of b_3 and can be assigned to $\beta^C\beta^B$ carbon in a CEB type triad of an EE**C**EB pentad sequence. However, the difference in chemical shifts between b_3 and b_4 are distinct in Figure 4b′, the difference between ^{13}C and ^1H chemical shift values of b_1 ($\alpha^C\delta^+$) and b_2 ($\alpha^C\gamma^B$) are not resolved.

Figure 4, parts c and c′, shows selected region from the f_2f_3 planes at $f_1 = 207.92$ ppm from the HC_AC_X and HC_AC_X−HH−TOCSY spectra. The plane from HC_AC_X spectrum, shows two H_A-C_A correlations c_1 and c_2 corresponding to methylene groups α to the carbonyl group, indicating that these peaks arise from two different triads on either side of the central C unit of an unsymmetrical pentad. The cross-peak labeled c_2 appears at $\delta_H = 2.28$ and $\delta_C = 42.66$ ppm, consistent with the shift of $\alpha^C\delta^+$ methylene groups in CEE/EEC triads. However, the label c_2 indicates that it is assigned to a CEE triad in WECEE pentad sequence based on the assignment of c_1 cross-peak. The c_2 cross-peak has a corresponding TOCSY correlation in the HC_AC_X−HH−TOCSY plane (c′) from a $\beta^C\delta^+$ methylene group at $\delta_H = 1.56$ ppm, confirming the assignment to CEE triads. The cross-peak c_1, $\delta_H = 2.39$ and $\delta_C = 40.36$ ppm is clearly a new correlation that is shifted upfield by ~2.4 ppm in the f_2 dimension compared to cross-peak of the symmetrical EECEE pentad sequence. This c_1 cross-peak is assigned to $\alpha^C\beta^B$ methylene groups of BEC triads in BECEE pentad sequences. This peak has corresponding TOCSY cross-peaks in the HC_AC_X−HH−TOCSY spectrum from nonequivalent $\beta^C\alpha^B$ methylene protons. Only one peak from the nonequivalent pair of protons is apparent at about $\delta_H = 1.88$ ppm, the other cross-peak of the pair is expected to appear at about $\delta_H = 1.80$ ppm, as evident from the HMBC spectrum of the poly(EBC*), but this cross-peak is missing from the 3D spectrum, probably due to insufficient magnetization transfer or nonoptimum mixing time.

Figure 4d and d′ shows selected regions from the f_2f_3 planes at $f_1 = 207.60$ ppm from the HC_AC_X and HC_AC_X−HH−TOCSY spectra. In plane d, two cross-peaks are identified at positions very similar to those observed in plane c. However, as in Figure 4a and b, the cross-peaks in this plane are from BECEB pentad sequences and thus the difference in their chemical shift compared to BECEE is minimal. In this plane, two cross-peaks, d_1 and d_2, appear at $\delta_H = 2.38$; $\delta_C = 40.37$ and $\delta_H = 2.29$; $\delta_C = 42.75$ ppm, respectively. Cross-peak d_2 is consistent with the shift of $\alpha^C\gamma^B$ methylene group of a CEB triad and this peak has corresponding TOCSY cross-peaks in the HC_AC_X−HH−TOCSY spectrum (d_4) consistent with the proton shift ($\delta_H = 1.64$ ppm) of $\beta^C\beta^B$ methylene groups, confirming the assignment to CEB triads. A second H_A-C_A correlations (d_1) at $\delta_H = 2.38$ ppm arises from the equivalent $\alpha^C\beta^B$ methylene protons from the BEC triad structures. This group has corresponding TOCSY cross-peaks in the HC_AC_X−HH−TOCSY spectrum from non-equivalent $\beta^C\alpha^B$ methylene protons. Only one peak from the pair of nonequivalent protons is apparent at about $\delta_H = 1.84$ ppm. In total, it is possible to unambiguously assign four different E**C**E centered pentad structures. Although HCACX−HH−TOCSY correlations show poor signal-to-noise for most of the β^C protons, it is sufficient to identify different cross-peaks at the pentad level. Chemical shift assignments for these pentads are summarized in Table 3.

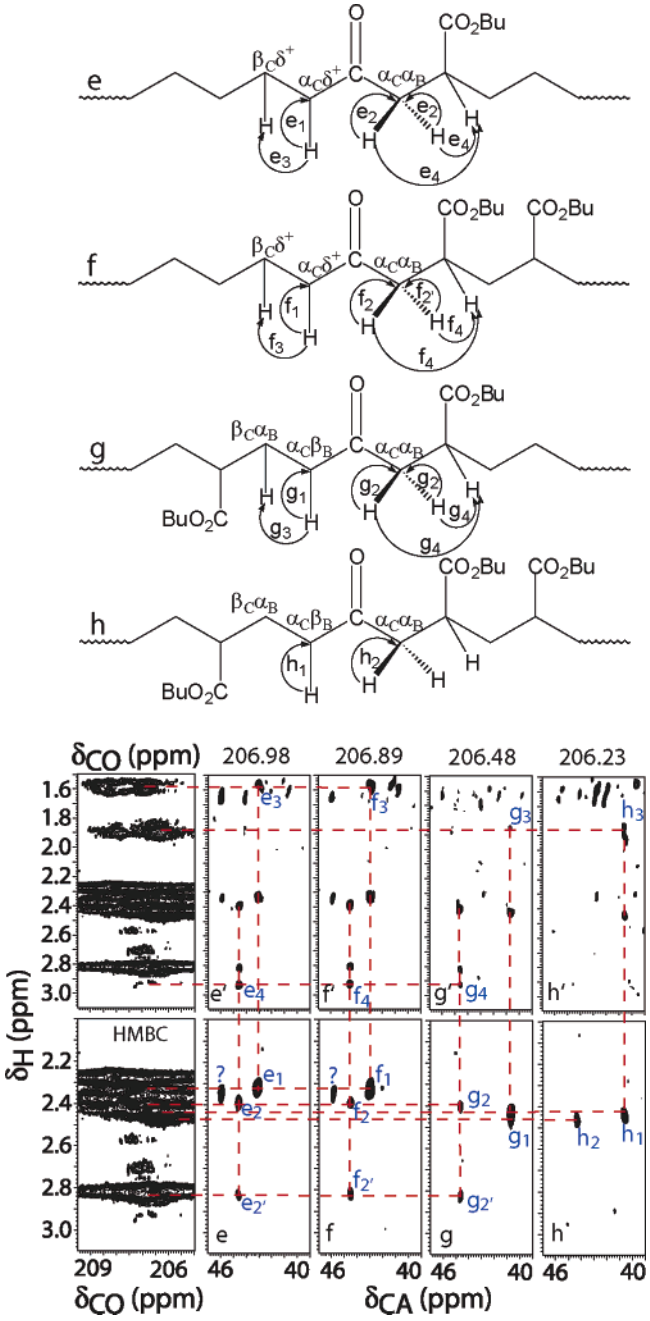


Figure 5. 2D $^1H-^{13}C$ HMBC (upper and lower left) and f_2f_3 planes from the 3D HC_AC_X (e−h) and HC_AC_X−HH−TOCSY (e′−h′) NMR spectra along with structures corresponding to individual pentad sequences: (e and e′) EECBE; (f and f ′) EECBB; (g and g′) BECBE; and (h and h′) BECBB pentads.

WECBZ Pentads. Figure 5 shows f_2f_3 planes corresponding to WE**C**BZ pentad sequences from 3D HC_AC_X (bottom, e−h) and HC_AC_X−HH−TOCSY (top, e′−h′) NMR spectra along with corresponding regions of HMBC NMR spectrum of poly-(EBC*). Also, pentad structure fragments showing correlations that are observed in the 3D NMR spectra are displayed on top of the figure. Four different sets of f_2f_3 planes are displayed corresponding to four different carbonyl shifts displayed on top of the each set of planes. The chemical shifts of identified cross-peaks are given in Table 3. Figure 5e shows selected regions from the f_2f_3 planes at $f_1 = 206.98$ ppm from the HC_AC_X 3D NMR spectrum. Three cross-peaks from this plane contain H_A-C_A correlations e_1, e_2, and $e_{2'}$ from methylene groups α to the carbonyl carbon. Out of three cross-peaks, two peaks, e_2 and $e_{2'}$, appear at the same carbon chemical shift ($\delta_C = 44.58$ ppm)

but different proton chemical shifts ($\delta_H = 2.38$ and 2.82 ppm). This pattern clearly indicates that these are two diastereotopic protons with a stereogenic center on the neighboring carbon. This is possible in the case of a **C**BE triad sequence in which $\alpha^C\alpha^B$ protons are diastereotopic in nature. This peak has a corresponding TOCSY cross-peak in the HC_AC_X−HH−TOCSY spectrum (e_4) consistent with a CH_{CBE} proton at $\delta_H = 2.94$ ppm, confirming that the cross-peaks e_2 and $e_{2'}$ in the HC_AC_X spectrum arise from CBE triad sequences. Moreover, cross-peak e_1 is consistent with the shift ($\delta_H = 2.33$; $\delta_C = 43.03$ ppm) of $\alpha^C\delta^+$ methylene group of a **C**EE/EE**C** triad and this peak has corresponding TOCSY cross-peak (a_3) in the HC_AC_X−HH−TOCSY spectrum consistent with the proton shift of $\beta^C\delta^+$ methylene groups, confirming the assignment to EE**C** triad. The slight downfield shift of the $\alpha^C\delta^+$ methylene carbon in the EE**C**BE pentad sequence in comparison to the EE**C**EE pentad sequence is due to the presence of *n*-butyl acrylate next to carbon monoxide carbon in the EE**C**BE sequence. Thus, the ^{13}C carbonyl shift e is assigned to EE**C**BE pentad. Although we observed a cross-peak (marked as "?") at $\delta_C = 46.01$ and $\delta_H = 2.33$ ppm, it is hard to explain the origin of this cross-peak from the present data. The chemical shift information suggests that the cross-peak might originate from some kind of branched structures in which there is CH branch point in the carbon position α to the carbonyl carbon. However, this is just an assumption and it cannot be proven; no such peaks are seen in the 2D HMBC spectrum.

Figure 5, parts f and f′, shows f_2f_3 planes at $f_1 = 206.89$ ppm from the 3D HC_AC_X and HC_AC_X−HH−TOCSY NMR spectra. Two regions from the plane #163 of the HC_AC_X spectrum, f_1 and $f_2/f_{2'}$, correspond to $\delta_{CO} = 206.90$ ppm (position f), contain H_A-C_A correlations. These regions contain correlation to protons with chemical shifts of 2.33, 2.39, and 2.82 ppm (cross-peaks f_1 and $f_2/f_{2'}$), respectively, indicating that these peaks are from different triads on either side of the central **C** unit. Cross-peak f_1 is consistent with the shift of $\alpha^C\delta^+$ methylene group ($\delta_H = 2.33$; $\delta_C = 42.98$ ppm) of a EE**C** triad and this peak has corresponding TOCSY cross-peaks in the HC_AC_X−HH−TOCSY spectrum (f_3) from a $\beta^C\delta^+$ methylene group ($\delta_H = 1.60$ ppm), confirming the assignment to EE**C** triads. A second region from plane # 163 contains H_A-C_A correlations (f_2 and $f_{2'}$) at $\delta_C = 44.50$ ppm which arise from the nonequivalent $\alpha^C\alpha^B$ methylene protons that can be assigned to a **C**BB triad structure. Mostly, the difference between the shift of $\alpha^C\alpha^B$ methylene groups in CBE and CBB triads is reflected in slight upfield shift (0.1 ppm) of $\alpha^C\alpha^B$ methylene carbon. This trend is consistent with the EBE and EBB shift pattern (Figure 4, parts a and b). Moreover, this peak has corresponding TOCSY cross-peaks in the HC_AC_X−HH−TOCSY spectrum (f_4) from the CH_{CBE} proton at $\delta_H = 2.93$ ppm. The cross-peak intensity for **C**BB triad unit should be half that of the **C**BE triad unit as shown in Table 3. However, the intensity patterns of cross-peaks in Figure 5, parts e and f, are almost equal and it might be due to bleed through of the **C**BE cross-peaks in **C**BB plane. The spectral pattern indicates that 206.90 ppm peak in the carbonyl region can be assigned to EE**C**BB pentad structures.

Parts g and g′ of Figure 5 show selected region from the f_2f_3 planes at $f_1 = 206.48$ ppm of the HC_AC_X and HC_AC_X−HH−TOCSY 3D spectra of poly(EBC*). Two regions from plane #176 of the HC_AC_X spectrum contain H_A-C_A correlations g_1, and $g_2/g_{2'}$ from methylene groups α to the carbonyl carbon. Two cross-peaks g_2 and $g_{2'}$ appear at $\delta_C = 44.64$ ppm and $\delta_H = 2.41$ and 2.83 ppm respectively, indicating their diastereotopic nature. As assigned above, these peaks are from **C**BE triad units showing correlations from nonequivalent $\alpha^C\alpha^B$ methylene protons to the $\alpha^C\alpha^B$ carbon. However, cross-peak g_1 is shifted upfield compared to the f_1 cross-peak and comparing the cross-peak pattern from Figure 4, it can be assigned to the shift of $\alpha^C\beta^B$ methylene carbon of a BE**C** triad. This cross-peak shows a corresponding TOCSY cross-peak in the HC_AC_X−HH−TOCSY spectrum (g_3) consistent with the proton shift of $\beta^C\alpha^B$ methylene proton, confirming the assignment to BE**C** triads in BE**C**BE pentad sequences.

Figure 5, parts h and h′, shows f_2f_3 planes at $f_1 = 206.23$ ppm from the HC_AC_X and HC_AC_X−HH−TOCSY 3D spectra. Two regions from the plane #184 of the HC_AC_X spectrum, h_1 and h_2 correspond to two very different carbons on either side of central carbonyl carbon. Cross-peak h_1 is consistent with the shift of $\alpha^C\beta^B$ methylene group of a BEC triad as described for Figure 5g. This peak has corresponding TOCSY cross-peaks in the HC_AC_X−HH−TOCSY spectrum (h_3) from a $\beta^C\alpha^B$ methylene proton at $\delta_H = 1.9$ ppm, confirming the assignment to BEC triad. Other cross-peak, h_2, in plane h, shows only one correlation at $\delta_C = 44.33$ and $\delta_H = 2.47$ ppm. There are no TOCSY cross-peaks in the HC_AC_X−HH−TOCSY spectrum. The cross-peak pattern indicates that the carbonyl carbon shift might be due to some kind of branching structures from BECB-(X)E type pentad sequence. A complete summary of the ^1H and ^{13}C resonance assignments obtained from these data are presented in Table 3. Also, high resolution PDF files of the figures used in this paper, as well as additional planes and resonance assignments are presented in the Supporting Information. This will permit the reader to examine the data more carefully than the printed figures allow.

Conclusion

In this work, it is demonstrated that the use of 3D HC_AC_X and HC_AC_X−HH−TOCSY NMR experiments provide increased spectral dispersion compared to a commonly used 2D-HSQC and HMBC methods. Application of ^{13}C labeling provides dramatic sensitivity improvements and selective filtering of resonances from undesired structures in the spectrum. Combined application of 3D NMR and ^{13}C labeling provide the spectral simplification, dispersion, and enhancement needed to assign the resonances of C-centered pentads in poly(ethylene-*co*-*n*-butyl acrylate-*co*-carbon monoxide) using ^{13}C-carbon monoxide labeled poly(EBC*). With this technique, unambiguous assignments of the resonances arising from eight carbonyl centered pentads are obtained. Although it is tempting to devise a set of equations for compositional analysis of this terpolymer system, the relative utility of different regions will be highly dependent on the exact composition of the polymers. While some of the assigned resonances will be useful for characterizing the specific polymers used in this work, commercial polymers having lower C or B content will require using different combinations of the assigned resonances presented here. For this reason, we are reluctant to recommend specific formulas for compositional analysis.

Not only is the spectral dispersion in these 3D spectra superior to that found in HSQC/HMQC and HMBC 2D experiments commonly used for polymer structure characterization; the 3D experiments rely on sequential magnetization transfer using large one-bond J couplings, permitting the collection of better spectra than those obtained from 2D HMBC experiments which rely on small, long-range J couplings. Unlike the HMBC experiments, the 3D experiments do not suffer from significant signal loss from relaxation effects. The identification of the structures present in this complex polymer and assignment of their

resonances will be useful for understanding process change effects on microstructure and property variations arising from differing microstructures. These techniques can also be extended to solve the complex structures problems involving hydrocarbon-based polymers, polymer chain-ends and mixtures of small organic molecules.

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Supporting Information Available: Figures showing copies of the 3D planes with assignments to 8 pentad structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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