246 *Macromolecules* **1997,** *30,* 246−256

# Short-Chain Branching Structures in Ethylene Copolymers Prepared by High-Pressure Free-Radical Polymerization: An NMR Analysis

**E. F. McCord, W. H. Shaw, Jr., and R. A. Hutchinson***

*Central Research and Development, Experimental Station, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware 19880-0101*

*Received May 10, 1996; Revised Manuscript Received October 11, 1996*⊗

ABSTRACT: It is well-known that short-chain branching (SCB) reactions (intramolecular H-abstraction) play an important role in determining the properties of ethylene homopolymers produced under high pressure by free-radical polymerization. There is little information, however, regarding SCB mechanisms that occur during the synthesis of ethylene copolymers under similar reaction conditions. This work describes SCB structures for a wide range of ethylene copolymers of varying composition (ethylene with *n*-butyl acrylate (nBA), methyl acrylate (MA), vinyl acetate (VAc), *n*-butyl methacrylate (nBMA), acrylic acid (AA), and methacrylic acid (MAA)), as determined by proton, $^{13}$C, and 2D NMR techniques. Close examination of the resonances reveals that for many (if not all) of these copolymers, a significant fraction of the SCBs contain comonomer as a result of $CH_2$-radical to $CH_2$ backbiting around a comonomer unit. In addition, SCBs are formed not only by hydrogen abstraction from $CH_2$ polyethylene units but also by abstraction of hydrogen from the comonomer methine units. This latter mechanism does not occur during production of E/VAc, E/nBMA, or E/MAA but is important for E/AA and acrylate (E/MA and E/nBA) copolymers; for these systems 10−20% of the comonomer groups in the polymer are alkylated. Implications of these findings to the polymerization kinetics are discussed.

## Introduction

The formation of short chain branches (SCB) long has been known to occur in high-pressure ethylene homopolymerization,[1] with the frequency of SCBs controlling polymer crystallinity and density.[2] Backbiting (SCB formation) is a type of intramolecular chain transfer in which the growing radical curls back on its own chain to form a six- or seven-membered intermediate ring, transferring the radical back along the chain by hydrogen atom abstraction. The result is a short-chain butyl or amyl branch. Shorter branches (methyl, ethyl, and propyl) are formed through double backbiting mechanisms.[3] The predominate SCB species formed are ethyl and butyl branches; amyl, methyl, and propyl species, formed via seven-membered rings, are less common.[4] SCB mechanisms leading to the formation of a butyl branch (denoted by $B_4$ and formed by a single backbite) and paired ethyl branches (denoted by $B_2$ and formed by a double backbite) are shown schematically as Figure 1.

Many ethylene copolymers are also synthesized at high pressures (20−40 kpsi) by free-radical processes. However, the role of comonomer in SCB reactions has not been examined to a great extent. This is primarily because the comonomer side groups (acrylate, acid, acetate) themselves act as effective SCB units; the type and number of comonomer groups control polymer properties to a much greater extent than branches formed by backbiting mechanisms.[2] Examination of backbiting mechanisms during copolymerization, however, provides valuable insights regarding these reaction systems.

The types of backbiting mechanisms that may occur during copolymerization are illustrated schematically in Figure 2, for six-membered intermediate rings in an ethylene/acrylate system:

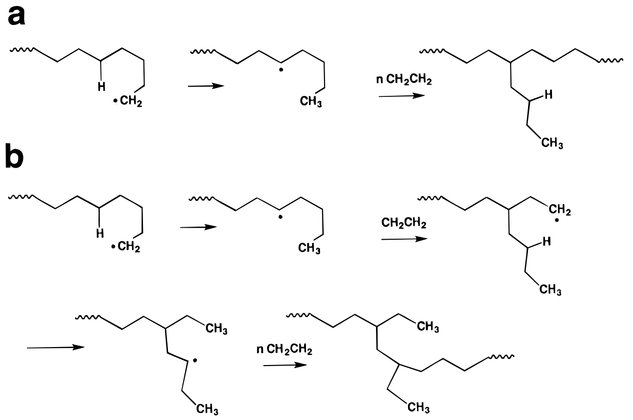

**Figure 1.** Typical short-chain branching mechanisms for ethylene homopolymerization: (a) formation of a butyl branch (single backbite); (b) formation of paired ethyl branches (double backbite).

> A comonomer radical may backbite and abstract hydrogen from a $CH_2$ unit. This structure is denoted as $A_1B_4$ to indicate that the acrylate group is found on the end (or "1") carbon of the resulting $B_4$ branch (Figure 2a).
>
> A $CH_2$ radical may backbite *around* a comonomer unit in the chain, to form an $A_3B_4$ butyl branch (Figure 2b).
>
> A $CH_2$ radical may abstract hydrogen from a comonomer unit to form a tertiary-centered radical structure. After subsequent chain growth, the resulting alkyl SCB is located opposite the comonomer side chain to form a quaternary carbon structure. The notation $A_QB_4$ is adopted to indicate that the butyl branch originates from a quaternary carbon with an opposing acrylate branch (Figure 2c).

These mechanisms illustrate cases in which only a single acrylate unit is involved. It is evident that other

---

* To whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1997.

S0024-9297(96)00687-0 CCC: $14.00

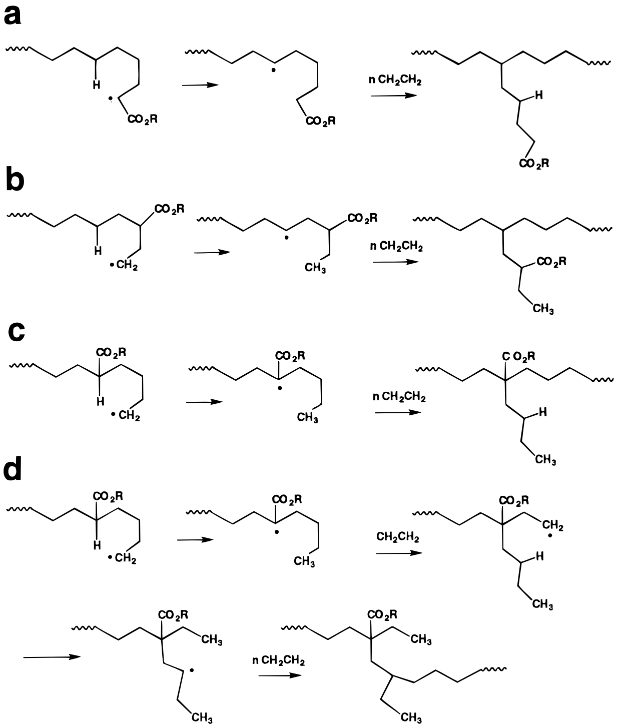

**Figure 2.** Possible short-chain branching mechanisms involving polymerization of ethylene with an acrylate comonomer: (a) H-abstraction by a comonomer radical (formation of $A_1B_4$ branch); (b) H-abstraction across a comonomer unit (formation of $A_3B_4$ branch); (c) H-abstraction from a comonomer unit to form $A_QB_4$ butyl branch (single backbite); (d) double-backbite mechanism involving H-abstraction from a comonomer unit, to form paired $A_QB_2-B_2$ branches.

butyl branch structures containing multiple acrylates, such as $A_3A_QB_4$, are also possible. In addition, double backbite mechanisms may result in $A_QB_2$ branches. Figure 2d outlines one mechanistic pathway to form an $A_QB_2$ and $B_2$ pair; alternate pathways to the same structure and even to the formation of paired $A_QB_2$ branches can be envisioned. The goal of this work is to determine which of these mechanisms are important during high-pressure copolymerization of ethylene with various comonomers, including *n*-butyl acrylate (nBA), *n*-butyl methacrylate (nBMA), vinyl acetate (VAc), methyl acrylate (MA), acrylic acid (AA), and methacrylic acid (MAA).

Although $^{13}$C NMR has proven to be a powerful tool for examining the types and quantities of SCBs found in homopolymers,[4−7] it has seen limited application to ethylene copolymers. The most widely examined copolymer system is E/VAc. Many of the studies examine copolymers synthesized at much lower temperatures and pressures than of interest to this work, and concentrate on monomer sequencing[8−11] or VAc monomer inversion[12,13] rather than short-chain branching. However, there are some issues discussed in the E/VAc literature which are pertinent to the present SCB study.

A few studies examine SCB levels by $^{13}$C for E/VAc copolymers produced at high pressures. Wagner *et al.*,[14] studying polymers up to 30 wt % VAc, found that total SCB level (number of $CH_3$ groups) is independent of VAc content, while the number of butyl branches decreases with increasing VAc content. Grenier-Loustalot[15] also studied SCB in E/VAc copolymers with 5−25 wt % VAc by $^{13}$C NMR, using model compounds to aid in peak assignments. Some of the same trends are observed; the number of butyl and amyl$^+$ (of length 5 or longer) branches decrease with increasing VAc level. In addition, it was found that the number of ethyl branches remains constant with VAc level. Contrary to the work of Wagner *et al.*, however, Grenier-Loustalot found that the total SCB level decreased significantly as VAc content in the polymer increased. The results of Okada *et al.*[16] and Bugada and Rudinrudin are in general agreement with those of Grenier-Loustalot, although Bugada and Rudin note a more pronounced decline in ethyl branch concentration with increasing VAc content in the polymer. All of these studies focus on alkyl branches and do not consider the role of comonomer in SCB mechanisms.

However, a careful examination of this previous work suggests that the presence of VAc may lead to additional SCB structures. In Grenier-Loustalot's $^{13}$C NMR study of E/VAc,[15] the ethyl $1B_2$ peak is observed at the expected location of 10.8 ppm (details on peak positions follow), but an additional peak is seen at 9.8 ppm for the polymer with the highest VAc level (25 wt %). Grenier-Loustalot does not identify this new structure but attributes the signal to a $1B_2$ branch. Okada *et al.*[16] report the presence of this additional peak at 9.8 ppm, and conclude that it can be attributed to the influence of an adjacent VAc unit on a $1B_2$ signal. Evidence supporting an alternative structure for this $^{13}$C NMR peak is presented in this work.

An issue that has been examined previously, albeit with conflicting results, is whether or not a propagating VAc radical backbites along the chain according to the mechanism shown in Figure 2a. Theoretical calculations[18] suggest that the formation of acetoxybutyl $A_1B_4$ branches is indeed possible, yet the evidence in the literature is mixed. Wisotsky *et al.*[19] used proton NMR to study copolymers synthesized at 80−150 °C; they saw no evidence of $CH_2OAc$ protons and concluded that VAc radicals do not participate in backbiting events. Amiya *et al.*,[13] however, do find evidence of acetoxyl-terminated short chain branches. This difference may be explained by examining details of the two studies; Wisotsky *et al.* studied polymers of 30−50 wt % VAc, while the study of Amiya *et al.* was for polymers of much higher (80−90 wt %) VAc content. Even at such high VAc levels, Amiya found that the number of alkyl branches was an order of magnitude higher than the number of acetoxyl branches. The presence or absence of $A_1B_4$ groups is further examined in this work.

Previous studies on other ethylene copolymer systems are even more scarce. Bruch and Payne[20] apply $^{13}$C NMR for the determination of monomer sequences in E/MA copolymers and terpolymers with CO. However, the work did not examine SCB. By far the most comprehensive reference pertinent to the present work is the NMR study of Randall *et al.*;[21,22] E/AN (acrylonitrile) copolymers are the main focus of the work, but results for E/AA, E/MA, and E/VAc are also reported. Abundant evidence supporting the abstraction of hydrogen from a comonomer unit (mechanisms of Figure 2c,d) is given; 23% of the comonomer units are alkylated for E/AN copolymer, 16% for E/AA, 10% for E/MA, and <3% for E/VAc. Branches with terminal AN groups were identified and were postulated to be formed by the mechanism shown as Figure 2a; corresponding structures for the other comonomers examined were not reported. No mention is made of branches that include the comonomer unit interior to the branch, as would be formed by the mechanism shown as Figure 2b.

The present effort builds upon the insightful work of Randall *et al.*,[21,22] using NMR techniques to determine the role that comonomer plays in short-chain branching mechanisms during high-pressure free-radical ethylene copolymerization. A systematic study of how SCB levels change as a function of polymer composition is presented for E/nBA, E/MA, and E/VAc; more limited data for E/nBMA, E/AA, and E/MAA systems complement the study and reinforce the conclusions. The different SCB structures seen for the acrylate, methacrylate, and VAc copolymers are discussed in terms of comonomer structure and relative radical reactivity.

## Experimental Section

All of the samples discussed in this work were synthesized in a well-mixed continuous-flow pilot-scale autoclave reactor at a single pressure level in the range typical for ethylene copolymer production. Conversion was in the range of 10−20%. Thus the level of short-chain branching formed by intramolecular reaction is only a function of reactor temperature, comonomer type, and copolymer composition. Synthesis temperatures of the various samples are included in the discussion of results.

$^{13}$C NMR (100 MHz) spectra were obtained on a Varian Unity 400 MHz spectrometer on 20 wt % polymer solutions and 0.05 M tris(acetylacetonato)chromium(III) (Cr(acac)$_3$) in 1,2,4-trichlorobenzene (TCB) unlocked. (For E/VAc samples, a mixed solvent of 6:1 TCB:benzene-$d_6$ was used and the spectrometer was run locked. This solvent mixture did not improve the resolution and is not necessarily recommended, since in some cases it may diminish polymer solubility.) Most samples were run at 120 °C, although a few ethylene homopolymer samples were run at 140 °C; no observable change in chemical shifts resulted from this difference. The spectrometer was run using a 90° pulse of 13.4−28.5 $\mu$s (two different probes were used), a spectral width (*sw*) of 35 kHz, a relaxation delay (*d*1) of 5 s, an acquisition time (*at*) of 0.45 s, and inverse-gated decoupling ($dm = nny$). $T_1$ (longitudinal magnetization relaxation time) measurements under similar conditions for similar polymers show that relaxation times for all carbons for these types of polymers under these conditions are all less than 1 s. Thus, the data are quantitative. Samples were preheated for at least 15 min before acquiring data. Data acquisition time was typically 12 h per sample. Spectra are referenced to the solvent (TCB) high-field resonance at 127.8 ppm. Integrals of unique carbons in each branch were measured and are reported as number of branches per 1000 CH$_2$ (including methylenes in the backbone and branches, but not the methylenes in the comonomer functional group). These integrals have a relative accuracy of ±5% for abundant branches and ±10−20% for branches present at less than 10 per 1000 CH$_2$. For the copolymer samples, the homopolymer convention of reporting branch numbers per 1000 CH$_2$ is maintained. To convert to the frequency per backbone unit, it is necessary to multiply the reported branch number by $1000/(1000 + A_{\mathrm{tot}})$, where $A_{\mathrm{tot}}$ is the tabulated number of comonomer units per 1000 CH$_2$.

Assignments shown on the NMR spectra are labeled according to the following naming scheme:

> $x$B$_y$: B$_y$ is a branch of length *y* carbons; *x* is the carbon being discussed, with the methyl at the end of the branch numbered as 1. Thus the second carbon from the end of a butyl branch is 2B$_4$. $x$B$_y{}^+$ refers to branches of length *y* and longer and includes end-of-chain (EOC) contributions.
>
> Greek symbols are used to designate the location of methylenes along the chain backbone. The first Greek letter gives the distance in carbon atoms to the nearest branch; thus $\beta$ refers to a backbone CH$_2$ two carbon units away from a branch point. If two letters are given, the second refers to the distance from a second branch point in the opposing direction. $\gamma^+$ refers to methylenes three or more units away from a branch point.
>
> $x$A$_z$B$_y$ refers to a branch containing a comonomer unit *A*, where *z* is the carbon carrying the comonomer functional group (following the same numbering pattern as *x*). Thus the SCB shown in Figure 2b is labeled A$_3$B$_4$. Consistent with homopolymer nomenclature, $x$A$_z$B$_y{}^+$ refers to branches of length *y* of longer, including EOC contributions.
>
> $x$A$_{\mathrm{Q}}$B$_y$ indicates that the comonomer unit is located off the backbone carbon at the branch point, making it quaternary. Thus the butyl branch shown in Figure 2c is labeled A$_{\mathrm{Q}}$B$_4$. If an alkyl group (rather than a comonomer group) is opposite the SCB, it is labeled R$_{\mathrm{Q}}$B$_y$.
>
> E$_x$, in copolymer spectra, refers to carbon group on the comonomer ester group, with E$_1$ the methyl group at the end.

Further details on homopolymer peak assignments and NMR analysis are found in the literature.[4−7] Discussion of copolymer peak assignments is included as part of the Results sections.

All of the polymers examined have number-average chain lengths (DP$_n$) in the range of 500−1000, giving a maximum EOC contribution of 1−2 per 1000 CH$_2$. Since acetone was used as a chain-transfer agent during synthesis of these polymers, it is expected that the actual number of chain ends contributing to the EOC $^{13}$C NMR signals discussed in this work is even lower.

2D NMR techniques were used on selected copolymer samples to aid in peak assignments. For E/nBA the HSQC−TOCSY (Heteronuclear Single Quantum Correlation−TOtal Correlation SpectroscopY) experiment was run using a 14 wt % solution of an E/nBA copolymer in 1,2,4-trichlorobenzene-$d_3$ at 120 °C on a Varian Unity 400 MHz spectrometer with a 5 mm Varian indirect detection probe. The low-field residual proton resonance of the TCB-$d_3$ solvent was referenced as 7.27 ppm. For the carbon reference, the center of the high-field triplet was set to 127.8 ppm. This gave the chemical shift of the E$_2$ butyl ester as 19.69 ppm; this shift was then changed to 19.22 ppm in the 2D data set to match the chemical shift for this sample observed in the one-dimensional $^{13}$C experiment (run at 120 °C in protonated TCB with 0.05 M Cr(acac)$_3$) for this resonance. This procedure adjusts for any consistent chemical shift change caused by interaction of the Cr(acac)$_3$ with the TCB-$d_3$ solvent or an isotope effect on the TCB chemical shift. The HSQC−TOCSY pulse sequence[23−25] from the Varian user library 4.3 was used after modifying the pulses in the BIRD nulling sequence.[26] This experiment was run with $at = 0.25$ s, proton $sw = 3194.4$ Hz, $^{13}$C $sw = 6217$ Hz, $d1 = 2.47$ s, 96 transients per increment, a BIRD null delay of 0.6 s, with trim pulses and a single homospoil pulse, a window period of 17 $\mu$s, an 18.3 $\mu$s spin lock pulse, a mix time of 60 ms, phase-sensitive, delay times optimized for a *jxh* (the proton−carbon one-bond scalar coupling constant) value of 130 Hz, and with 128 increments in each phase set. The data set was processed using Gaussian functions, linear prediction, and was zero-filled. An HSQC experiment was run under identical conditions on the same sample using the same pulse sequence with the TOCSY period eliminated.

The E/VAc HSQC−TOCSY experiment was run using a 21 wt % solution in TCB-$d_3$ at 120 °C, using the hsmqc pulse sequence in the Varian user library 5.1.[26] Parameters were as described above, with the following slight changes: $at = 0.18$ s, proton $sw = 3199.5$ Hz, $^{13}$C $sw = 8045.1$ Hz, $d1 = 2.1$ s, a null delay of 0.9 s, and 128 transients per increment.

The E/MMA sample (converted from E/MAA by methyl esterification) HSQC and HSQC−TOCSY experiments were run on a 21 wt % solution in TCB-$d_3$ at 120 °C, using parameters similar to those described above (mix time of 80 ms, no window, 24 $\mu$s spin lock pulse, no homospoil pulse, proton $sw = 4514.7$ Hz, $^{13}$C $sw = 6441.2$ Hz, $at = 0.227$ s, $d1 = 0.7$ s, a null delay of 0.54 s, $jxh = 130$). These experiments were run on a Unity Plus 500 MHz Varian NMR using a 5 mm indirect detection probe. A gradient HMBC (Heteronuclear Multiple Bond Correlation) experiment was run on the same instrument using a gradient indirect detection probe at 75 °C, $at = 0.176$ s, proton $sw = 3999.6$ Hz, and $^{13}$C $sw =$

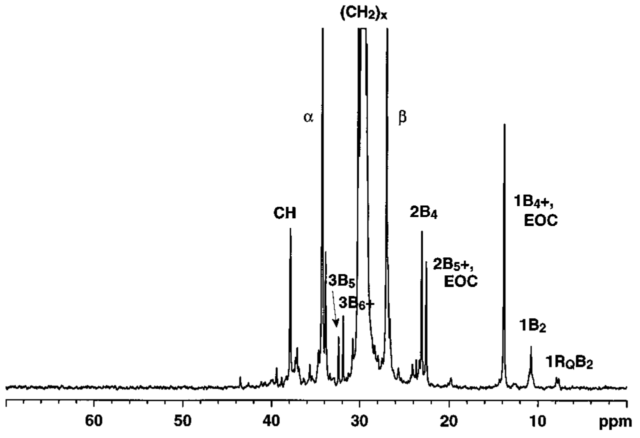

**Figure 3.** $^{13}$C NMR spectrum for ethylene homopolymer synthesized at 270 °C.

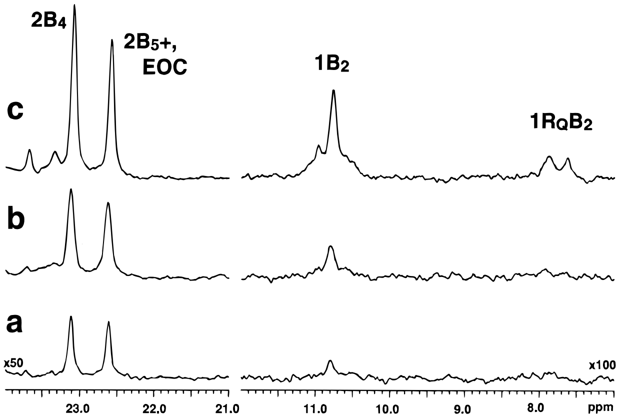

**Figure 4.** Details of 7−12 and 21−24 ppm regions from $^{13}$C NMR spectrum for ethylene homopolymer synthesized at (a) 165, (b) 195, and (c) 270 °C.

25141.4 Hz. The experiment was run with 256 increments and 80 transients per increment. Values of *j* for directly bonded carbons of 130 Hz and for multiple bond correlations of 9 Hz were used to calculate delay times. Other parameters include $d1 = 1.5$ s, no null, and no homospoil pulses. 2D data were processed using linear prediction, zero filling, and sine bell or Gaussian functions.

## Results

**Ethylene Homopolymer.** It is very useful to examine $^{13}$C NMR spectra for ethylene homopolymers, since these serve as references to the copolymer spectra examined later. The level of SCB (branches of length 5 or shorter) increases from about 6 per 1000 $CH_2$ for polymer produced at 165 °C to 20 branches for polymer synthesized at 270 °C, in agreement with well-documented trends in the literature.[2,27] Figure 3 shows the $^{13}$C NMR spectrum for the 270 °C sample, which has the highest level of SCB. Peak assignments shown on this figure were made in accordance with the literature.[4−7]

For purposes of comparison with copolymer results, the portions of the spectra of most interest are 7−12 ppm (ethyl branch structures) and 21−24 ppm ($2B_4$ butyl and $2B_5^+$ amyl$^+$ branch structures). Figure 4 shows these regions for homopolymer samples produced at 165, 195, and 270 °C. It can be seen clearly how peak intensities increase with polymer synthesis temperature. (Branch concentration is proportional to peak area.) Of particular interest is the emergence of the peak at 7.5−8 ppm, assigned to the formation of a $1R_QB_2$ quaternary-ethyl branch.[4] This peak is not observable for the 165 °C polymer, is barely discernible at 195 °C, and is very evident in the polymer produced at 270 °C. (The peak splitting seen at 270 °C has been attributed to racemic mixtures of the paired ethyl branches.[4]) This quaternary-ethyl structure can be formed either by a triple-backbiting mechanism or by intermolecular transfer (long-chain branching).[4]

In the ethylene homopolymer samples examined, only trace quantities of methyl and propyl branches are observed. Since these branches, which are formed by double-backbiting mechanisms involving seven-membered ring transition states,[4] are so rare in homopolymer, they are not considered in the discussion of copolymerization SCB mechanisms below. More complex structures, such as 5-ethylhexyl branches have been calculated to be possible at equal probability to paired ethyl branches[28,29] but have been experimentally found only in much smaller quantities.[6,30,31] These branches are difficult to detect with $^{13}$C NMR techniques[4] and also will not be considered further in this work. Instead, we focus on the more abundant ethyl and butyl branch structures which, as shown in Figure 2, are more likely to involve comonomer methine hydrogens.

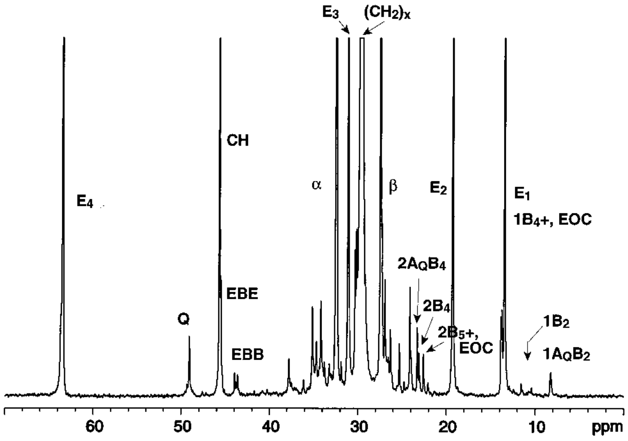

**Figure 5.** $^{13}$C NMR spectrum for E/nBA copolymer (34 wt % nBA) synthesized at 200 °C.

**E/nBA.** E/nBA copolymers of varying composition were synthesized at 165 and 200 °C and examined with $^{13}$C NMR. Figure 5 shows the spectrum for a 34 wt % nBA copolymer produced at 200 °C, with peak assignments as indicated. Comparison with the homopolymer spectrum of Figure 3 shows that:

> Some of the SCB information is lost because of peaks associated with the butyl ester of the acrylate ($E_x$) and adjacent backbone methylene. These include the $3B_5$ amyl, $1B_4^+$ butyl$^+$, and $3B_6^+$ hexyl$^+$ peaks.
>
> The SCB peaks observed for the homopolymer that are also seen in the copolymer spectrum are the $1B_2$ ethyl peak at 10.8 ppm, the $2B_5^+$ amyl$^+$ peak at 22.6 ppm, and the $2B_4$ butyl peak at 23.1 ppm.
>
> There are two resonances in the 23 ppm region of the $2B_4$ peak. It is argued that the second resonance, which is not seen for homopolymer, is due to butyl SCBs which have an opposing acrylate group ($2A_QB_4$).
>
> It is believed that the resonance structure at 8−8.5 ppm is from ethyl SCBs which have an opposing acrylate group ($1A_QB_2$).
>
> Indication about nBA sequences are contained in the 40−50 ppm shift region. In particular, the

**Table 1. SCB Structures in E/nBA from $^{13}$C NMR Analysis**[a]

| $T_{rct}$ (°C) | $w_p^{nBA}$ | $nBA_{tot}$ | $nBA_{qu}$ | $1B_2$, $1A_3B_4$ | $1A_QB_2$ | $2B_4$ | $2A_QB_4$ | $2B_5^+$ | $SCB_{tot}$ |
|---|---|---|---|---|---|---|---|---|---|
| 165 | 0.000 | 0 | 0 | 0.9 | 0 | 3.3 | 0 | 3.2 | 7.4 |
| 165 | 0.244 | 34 | 3.9 | 1.3 | 1.8 | 2.2 | 2.4 | 2.2 | 9.9 |
| 165 | 0.470 | 88 | 9.6 | 2.4 | 3.5 | 1.2 | 4.4 | 1.5 | 13.0 |
| 165 | 0.480 | 92 | 10.5 | 3.3 | 4.1 | 1.0 | 5.0 | 1.5 | 14.9 |
| 195 | 0.000 | 0 | 0 | 1.7 | 0 | 4.3 | 0 | 3.7 | 9.7 |
| 200 | 0.221 | 30 | 4.2 | 2.3 | 2.0 | 2.9 | 2.2 | 2.2 | 11.6 |
| 200 | 0.347 | 55 | 7.4 | 3.0 | 3.5 | 2.2 | 3.3 | 1.7 | 13.7 |
| 200 | 0.531 | 110 | 13.2 | 4.1 | 6.1 | 1.8 | 4.4 | 1.0 | 17.4 |

[a] All numbers (columns 3−10) per 1000 $CH_2$ units, excluding those in the ester group.

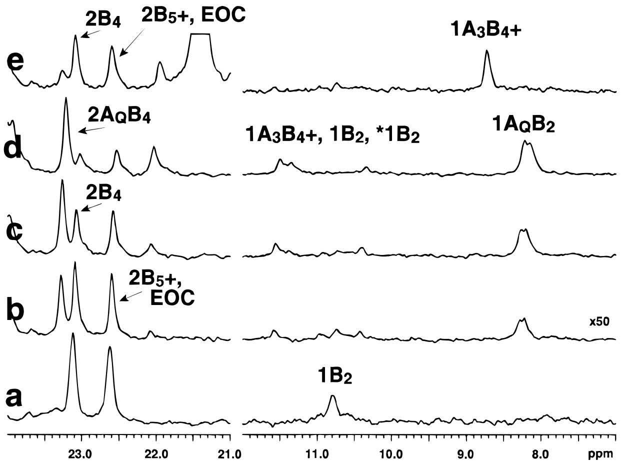

**Figure 6.** Details of 7−12 and 21−24 ppm regions from $^{13}$C NMR spectrum for (a) ethylene homopolymer (synthesized at 195 °C), (b) E/22 wt % nBA (200 °C), (c) E/35 wt % nBA (200 °C), (d) E/53 wt % nBA (200 °C), and (e) E/33 wt % nBMA (190 °C).

fraction of nBA-centered triads (EBE and EBB) can be calculated from the peaks indicated; no signal from BBB triads was observed for this sample.

The fraction of nBA units which are alkylated is also calculated from the 40−50 ppm shift region, with the quaternary acrylate carbon giving a signal at 49 ppm, as reported in the literature.[32] The assignment of this carbon has also been confirmed by DEPT (Distortionless Enhancement by Polarization Transfer) and off-resonance decoupling techniques. This signal gives a measure of the fraction of nBA units which have undergone hydrogen abstraction during polymerization—either by short- or long-chain branching.

A complete summary of the NMR analysis is contained in Table 1; further details about the analysis follow. In Table 1, the total number of nBA units ($nBA_{tot}$) is easily calculated from polymer composition, while $nBA_{qu}$ is simply that number multiplied by the fraction of alkylated nBA units, as measured by the quaternary carbon signal at 49 ppm.

Before analyzing the trends in Table 1, further discussion regarding the peak assignments is warranted. It is very instructive to examine in more detail the regions of the spectra containing information about ethyl branches (7−12 ppm) and butyl and amyl$^+$ branches (21−24 ppm). Figure 6 compares these areas for E/nBA copolymers synthesized at 200 °C (Figure 6b−d) with homopolymer produced at 195 °C (Figure 6a). (Figure 6e is for an E/nBMA copolymer sample, to be discussed later.) It can be seen that the ethyl (7−12 ppm) and butyl (23−23.5 ppm) branch structures increase with nBA content, while the amyl$^+$ branch concentration decreases. Some of the peak positions are shifted relative to homopolymer; these relative shifts, as well as how the peak intensities vary with nBA level in the copolymer, are the keys to deducing the polymer microstructure.

The downfield butyl peak in the 23−23.5 ppm range increases while the upfield peak decreases in height with increasing nBA level. The two peaks have been deconvoluted to obtain the estimates of relative intensity included in Table 1. Comparison with the homopolymer sample shows that the upfield peak can be assigned to $2B_4$; the downfield peak has been assigned to a butyl SCB with an opposing acrylate side group, labeled $2A_QB_4$. The small shift of 0.2 ppm is consistent with the effect of a substitution at the backbone carbon for this structure. The quaternary structure has been assigned to an acrylate side group (rather than another alkyl group) since the signal is not seen for homopolymer produced at the same conditions, and since its intensity increases with nBA level in the polymer. A similar $2B_4$ to $2A_QB_4$ shift was noted by Randall *et al.*[21,22] in their examination of E/AN copolymers.

No corresponding peak splitting is seen for the $2B_5^+$ peak. Although ethylene homopolymer contains amyl branches, an $A_QB_5$ SCB is very unlikely. Such structures would be formed via a seven-membered ring backbiting mechanism, with the acrylate group located on the sixth carbon from the radical end. This configuration is not possible without invoking monomer inversion, which is not likely for nBA.

Evidence for an $A_QB_2$ structure can also be seen in Figure 6, by examining differences in the spectra in the 8−12 ppm shift region for the E/nBA copolymers relative to homopolymer. For homopolymer, the $1B_2$ peak occurs at 10.8 ppm; for E/nBA copolymer, a peak at 8.3 ppm is seen, with intensity increasing with increasing nBA content. Furthermore, this new peak is at a different position than the $1R_QB_2$ peak (7.8 ppm) observed for homopolymer produced at high temperature (see Figure 4c). Note also that homopolymer produced at 195 °C (Figure 6a) shows little evidence of the $1R_QB_2$ peak, strengthening the conclusion that the peak observed in the E/nBA copolymers cannot be attributed to this structure. All indications (peak position, trend with copolymer composition) suggest the peak is for $1A_QB_2$, an ethyl branch with an opposing acrylate side group formed through a double-backbite mechanism shown as Figure 2d. Randall *et al.*[21,22] predict the presence of this peak, but do not observe it in the E/AN system; their arguments for the $A_QB_2$ structure are based upon other evidence.

Confirmation of these assignments has been obtained in a 2D HSQC−TOCSY $^1$H−$^{13}$C NMR correlation experiment. In this experiment, correlations from any observed proton to all protonated carbons in the neighborhood of that proton can be observed. The size of the neighborhood is determined by the length of the mixing time used in the TOCSY part of the experiment. Figure 7 shows the results for the 53 wt % nBA copolymer sample of Figure 6d.

In this figure, the vertical axis is proton NMR data, and the horizontal axis is $^{13}$C NMR data. The spectra shown along the axes are the corresponding 1D NMR data. As described in the Experimental Section, Cr(acac)$_3$ was not used in this 2D experiment, although it was used in all 1D $^{13}$C experiments in this work. No

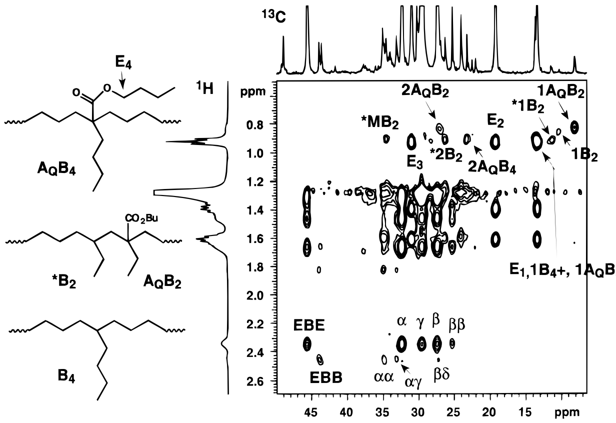

**Figure 7.** $^1H-^{13}C$ 400 MHz 2D NMR HSQC−TOCSY correlation spectrum for E/nBA copolymer of Figure 6d (53 wt % nBA).

evidence of selective relative chemical shift changes due to the presence or absence of $Cr(acac)_3$ was found, in agreement with other work.[33] Carbon correlations at 8.2 and 27.1 ppm from the $^1H$ methyl at 0.83 ppm can be seen. These are assigned to the $1A_QB_2$ and $2A_QB_2$ carbons, respectively. Close examination of the trace shows no further correlations along this row, even though the signal to noise ratio is adequate and the mix time is long enough (60 ms) to observe all carbon correlations in the four-carbon butyl ester fragment. This is exactly as would be expected—the third carbon in the $A_QB_2$ branch is a quaternary carbon, not observable in this HSQC−TOCSY experiment. Correlations to the $B_2$ half of $A_QB_2-B_2$ paired branches (formed by the mechanism in Figure 2d) are shown along the proton methyl row at 0.92 ppm. These are labeled with an asterisk to indicate that the other ethyl branch in the pair is $A_QB_2$, rather than $B_2$. Correlations are indicated to the carbons $*1B_2$, $*2B_2$, and tentatively $*MB_2$ (where M indicates the methine carbon of the branch). The different chemical shifts of $2A_QB_2$ and $*2B_2$ also support these assignments. There are correlations from many different kinds of methyls overlapping along this row; three correlations to the butyl ester methyl are marked as $E_1$, $E_2$, and $E_3$.

Confirmation that the methylene assigned to $2A_QB_4$ is indeed part of a short chain branch is also shown in this HSQC−TOCSY experiment. Although the $1A_QB_4$ carbon is overlapped by $E_1$, the $2A_QB_4$ resonance correlation to the methyl protons can be observed. Further methylene carbon correlations to the $A_QB_4$ methyl are not observed. A very small single correlation at about 7.8 ppm is assigned to $1B_2$ in a pair of $B_2$ ethyl branches not involving an acrylate group.

Perhaps the strongest argument supporting the claim that H-abstraction from the nBA group through backbiting occurs frequently is the unity of the evidence. SCB levels as a function of composition are plotted in Figure 8. Although the total number of SCBs (Figure 8a) is increasing with nBA content, a significant number of these branches are the result of hydrogen abstraction from a comonomer unit. Figure 8b contains two measures of alkylated nBA groups; the first is calculated from the quaternary carbon signal at 49 ppm ($nBA_{qu}$ from Table 1), and the second is calculated by summing the $2A_QB_4$ and $1A_QB_2$ contributions discussed previously. The two numbers are in very good agreement, with the difference possibly a measure of long-chain branch points at nBA groups or quaternary 5-ethylhexyl branches. Finally, Figure 8c plots the number of SCB

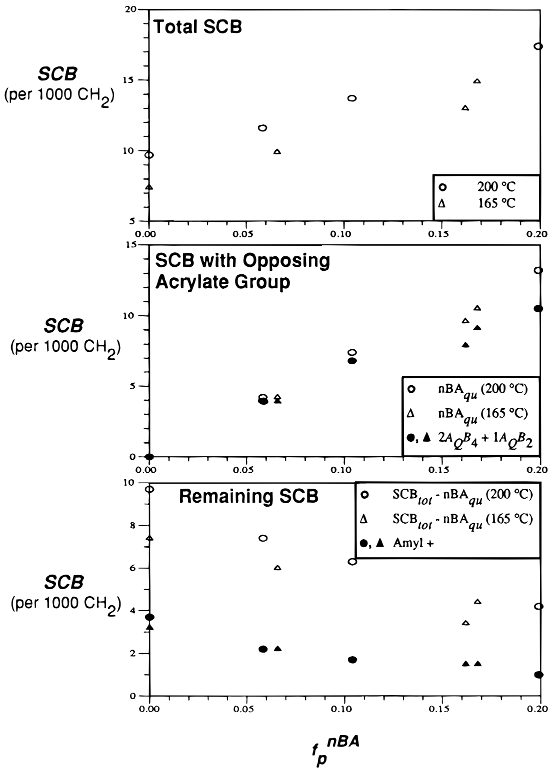

**Figure 8.** SCB in E/nBA copolymers as a function of mole fraction nBA in copolymer. See Table 1 and text for definitions.

that do not have an opposing acrylate group, as calculated by ($SCB_{tot} - nBA_{qu}$). This quantity represents the number of SCBs formed by H-abstraction from a $CH_2$ group and decreases with increasing nBA content in the polymer, as would be expected simply from composition arguments. A decrease in the number of $amyl^+$ branches is also seen; as previously discussed, formation of amyl branches cannot occur opposite an acrylate group since the branches are produced via a seven-membered backbiting ring. (For homopolymer, a large fraction of the $amyl^+$ signal comes from branches of length 6 or greater. Although the signal can include chain ends, the contribution is expected to be small since the polymers were synthesized with acetone present as a chain-transfer agent.) It is clearly evident that H-abstraction from an nBA group is much more prevalent than from a $CH_2$ group; over 10% of the nBA groups are quaternary, whereas in homopolymer at the same temperature, the short chain branching level is only 2−4% (10−20 SCBs per 1000 $CH_2$).

We next turn our attention to the questions of whether nBA radicals can themselves participate in backbiting mechanisms (Figure 2a) and if backbiting can occur around an nBA unit (Figure 2b). The four branch methylenes of the $A_1B_4$ branch should have $^{13}C$ chemical shifts of about 34.1 ($1A_1B_4$, based upon a measured value for methyl eicosenoate), 25.5−26.1 ($2A_1B_4$, based on either a $\beta$ COOR substituent value of +3 added to a butyl branch $2B_4$ methylene at 23.1 or a $\delta$ substituent value of +0.6 for the 3-carbon of methyl eicosenoate), 28.0 ($3A_1B_4$, based on a $\gamma$ COOR substituent added to a $3B_4$ carbon at about 30), and 34.8 ppm ($4A_1B_4$, based on a $\gamma$ substituent value of 0.6 added to a $4B_4$ carbon at 34.2).[34] There are other $^{13}C$ NMR signals from the polymer in these regions which might obscure the $A_1B_4$ resonances, if they are present. The protons of the methylene adjacent to the carbonyl carbon of the ester should be at about 2.25 ppm. This area is also obscured by other resonances in the proton spectrum of this polymer (for example, from acetone-derived ketone end groups). However, in the 2D NMR spectrum, this possible signal is free of interferences—no other correlations are expected in the region of $^{1}H = 2.25$ ppm and $^{13}C = 34.1$ ppm. As seen in Figure 7, no peaks are seen in this area. Since other methyl correlations ($1A_QB_2$ and $*1B_2$) are seen when present at levels of 3 per 1000 $CH_2$, it can be concluded that $A_1B_4$ branches, if present at all, are at a level of less than 2 per 1000 $CH_2$. The 2D correlation for the related $1A_1B_2$ structure was also not observed in the expected 31.2 ppm $^{13}C$ by 2.25 ppm $^{1}H$ region.

The second question—whether the mechanism shown as Figure 2b occurs—cannot be definitively answered for E/nBA. There is some direct evidence that it does occur, as seen by subtle differences in the ethyl peak region (10.5−11.5 ppm) in Figure 6. For homopolymer, the $1B_2$ peak occurs at 10.8 ppm. For E/nBA copolymer, multiple peaks are present in this region, with a definite peak occurring at 11.5 ppm and growing with increasing nBA content. These peaks could result from the the influence of an $1A_QB_2$ structure on the paired $1B_2$ ethyl branch. Alternatively, as also indicated on Figure 6, the peaks could indicate the presence of a $A_3B_4$ structure. (Note that the peak for $1A_3B_4$ cannot be differentiated from longer branches or chain ends; thus, on Figure 6 the structure is labeled $1A_3B_4^{+}$.) Even though $A_3B_4$ is a substituted butyl branch, it gives a signal in the 11 ppm range due to the presence of the acrylate group on the side chain. At this time, the exact structures leading to the extra peaks in the 11 ppm region are not known; in Table 1, the contributions are all included under the heading “$1B_2$, $1A_3B_4$”. It should be noted that if $A_3B_4$ branches are formed, they are likely to convert to paired $B_2-A_QB_2$ ethyl branches through a second backbite, because of the higher reactivity of the methine proton.

According to the backbiting mechanisms, ethyl branches will always occur in pairs. Thus for a $B_2-A_QB_2$ pair, the overall intensity in the 10−12 ppm region should be equal to the signal at 8.25 ppm; if additional resonances (e.g., $A_3B_4$) are present, the signal in the 10−12 ppm region should be greater than the 8.25 ppm signal for $1A_QB_2$. As can be seen from Table 1, however, the $1B_2$ level (which includes all peaks in the 10−12 ppm region) is usually less than that of $1A_QB_2$. This may be due to tacticity effects leading to multiple small peaks at low signal intensity.[4] In addition, mechanistic pathways for paired $1A_QB_2$ structures from nBA diads can be constructed, which would give signals only in the 8 ppm region.

**E/nBMA.** Additional verification of these mechanistic arguments and NMR assignations for E/nBA is obtained by a comparison with E/nBMA copolymer. The 7−12 and 21−24 ppm portions of the $^{13}C$ NMR spectrum for a 33 wt % nBMA copolymer synthesized at 190 °C are included as part of Figure 6. Significant differences are expected, since nBMA has a $CH_3$ unit opposite the acrylate side group rather than an extractable hydrogen. The E/nBMA (Figure 6e) spectrum can be directly compared with a E/nBA copolymer of similar composition and synthesis temperature (Figure 6c). It is seen that:

> The major fraction of the E/nBMA butyl peak at 23 ppm is located at the same position as the $2B_4$ homopolymer peak, rather than at the shifted position seen for E/nBA. This is to be expected, since nBMA does not provide an extractable hydrogen for the formation of a $A_QB_4$ structure. The cause of the downfield side peak off the E/nBMA butyl peak is presently unknown, although $2A_5B_5^{+}$ (including end groups) and $2R_QB_4$ structures would give a signal in this region.

**Table 2. SCB Structures in E/MA from $^{13}C$ NMR Analysis[a]**

| $w_p^{MA}$ | $MA_{tot}$ | $MA_{qu}$ | $1B_2$, $1A_3B_4$ | $1A_QB_2$ | $2B_4$ | $2A_QB_4$ | $2B_5^{+}$ | $SCB_{tot}$ |
|---|---|---|---|---|---|---|---|---|
| 0.000 | 0 | 0 | 0.9 | 0 | 3.3 | 0 | 3.2 | 7.4 |
| 0.238 | 48 | 6.1 | 3.0 | 3.2 | 2.7 | 3.5 | 2.8 | 15.2 |
| 0.370 | 87 | 9.5 | 4.1 | 5.4 | 1.2 | 4.4 | 1.9 | 17.0 |
| 0.493 | 137 | 14.9 | 4.4 | 6.5 | 0.5 | 5.3 | 0.9 | 17.6 |
| 0.590 | 190 | 16.9 | 4.9 | 6.3 | 0.1 | 4.9 | 0.3 | 16.5 |
| 0.637 | 222 | 18.2 | 5.3 | 6.6 | 0.1 | 6.2 | 1.8 | 20.0 |
| 0.739 | 316 | 15.1 | 9.0 | 8.0 | 0.0 | 2.2 | 0.3 | 19.5 |

[a] All numbers (columns 2−9) per 1000 $CH_2$ units.

> The E/nBMA polymer shows no sign of a $1A_QB_2$ peak at 8.25 ppm. A new peak, however, is observed at 8.9 ppm which has been assigned to a $1A_3B_4^{+}$ branch containing an nBMA unit. Since the signal strength of 3.1 occurrences per 1000 $CH_2$ units is much greater than is explained by end-of-chain contributions, it may be concluded that the bulk of the signal must be from $A_3B_4$ branches, formed by the mechanism shown as Figure 2b. The $1A_3B_4^{+}$ peak for E/nBMA gives a signal in the 9 ppm region since the 3-carbon is quaternary; the equivalent E/nBA structure gives a $^{13}C$ NMR signal at roughly 11.5 ppm where, as discussed earlier, several small peaks are observed which are not present for ethylene homopolymer or E/nBMA. Further evidence supporting the $A_3B_4$ assignment is found in 2D NMR experiments for E/MMA (methylated E/MAA) copolymer, as presented later.

> The methyl carbon of the $A_1B_4$ structure would be expected to have a $^{13}C$ NMR chemical shift of about 17.1 ppm. No methyl groups are observed in this region.

> For the E/nBMA sample, there are 1.6 ethyl ($1B_2$) branches, 3.7 ($2B_4$) butyl branches, 2.2 amyl+ ($2B_5^{+}$) branches, and a total of 10.6 SCB per 1000 $CH_2$ (3.1 from the peak at 8.9 ppm). These numbers are in reasonable agreement with the corresponding 195 °C homopolymer from Table 1, as would be expected for a polymer containing only 9 mol % comonomer.

These E/nBMA results provide a clear contrast to the E/nBA case. The presence of the methyl group eliminates the possibility of backbites occurring to nBMA units in the chain; corresponding backbites in the E/nBA system are plentiful. Clear evidence showing the presence of nBMA-containing SCBs is seen; these branches can be formed from the backbiting mechanism shown as Figure 2b. Although less convincing, NMR evidence for similar E/nBA $A_3B_4$ branches was also found. Finally, it can be concluded that, within spectroscopic detection limits, neither nBA- nor nBMA-ended radicals participate in SCB mechanisms (Figure 2a).

**E/MA.** It is expected that E/MA copolymers should show the same structures as observed for E/nBA. As summarized in Table 2, the results and trends with polymer composition are similar. All compositions were produced at similar temperatures, and the nomenclature is as in Table 1. The 7−12 and 21−24 ppm portions

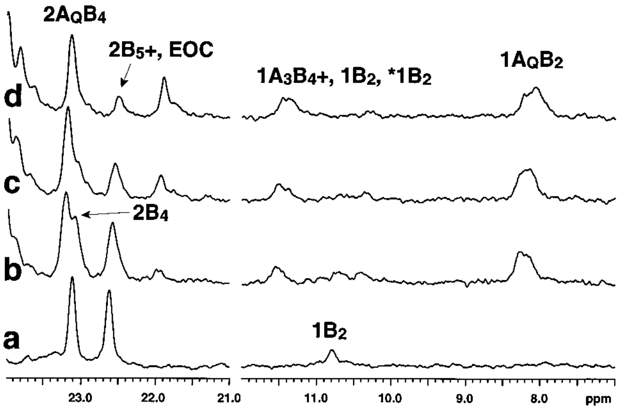

**Figure 9.** Details of 7−12 and 21−24 ppm regions from $^{13}$C NMR spectrum for E/MA copolymers: (a) ethylene homopolymer; (b) 24 wt % MA; (c) 37 wt % MA; (d) 49 wt % MA.

of the $^{13}$C NMR spectra for a subset of the data are shown as Figure 9.

As observed for E/nBA, SCB$_{tot}$ increases with increasing comonomer content, as do 1B$_2$ (and/or 1A$_3$B$_4$), 1A$_Q$B$_2$, and 2A$_Q$B$_4$ levels; amyl$^+$ branching decreases. All of the results can be explained using the backbiting mechanisms shown in Figure 2. The structures indicated by the 1A$_Q$B$_2$ and 2A$_Q$B$_4$ signals are formed by backbiting from the acrylate methine unit; the A$_Q$B$_4$ (2A$_Q$B$_4$ signal) branch is formed from a single backbite (Figure 2c), while the A$_Q$B$_2$ ethyl (1A$_Q$B$_2$ signal) branch is formed from a double backbite (Figure 2d). The main portion of the "1B$_2$, 1A$_3$B$_4$" signal is observed at 11.5 ppm, a different position than the 1B$_2$ peak of ethylene homopolymer. As discussed for E/nBA, this signal may be from an A$_3$B$_4$ structure (formed through the mechanism shown as Figure 2b), but may also be explained through the influence of an A$_Q$B$_2$ branch on the paired 1B$_2$ signal. HSQC and HSQC−TOCSY 2D experiments on E/MA gave identical results for those shown in Figure 7 for E/nBA. For E/MA, the expected peaks from the correlations of $^{13}$C 1B$_4$$^+$ and 1A$_Q$B$_4$ with the $^1$H methyl region are observed; these peaks are hidden under the nBA E$_1$ signal in Figure 7.

A closer examination of Table 2 reveals that the number of quaternary branches (1A$_Q$B$_2$ and 2A$_Q$B$_4$) reaches a plateau or even decreases at high MA levels; the same is observed for the number of alkylated MA units (MA$_{qu}$). This plateau/decrease at high MA content is easily explained by mechanistic arguments. These E/MA copolymers contain a much higher comonomer mole fraction (74 wt % MA copolymer = 57 mol%) than the E/nBA copolymers examined. In order to form an A$_Q$B$_4$ structure, it is necessary to have two ethylene units at the propagating chain end; this probability decreases as the MA content in the polymer increases. Similarly, as the ethylene content of the polymer decreases, a smaller fraction of the growing chains in the system will end in an ethylene-radical, decreasing the number of total SCB events and the number of MA units which become alkylated.

**E/VAc.** In contrast to the acrylate copolymers, E/VAc shows branching structures more similar to homopolymer. Polymers of varying composition were synthesized at 165 and 200 °C and analyzed by $^{13}$C NMR, with the results summarized in Table 3. Figure 10 shows some of the E/VAc results for the 200 °C samples in the key 7−12 and 21−24 ppm regions.

**Table 3. SCB Structures in E/VAc from $^{13}$C NMR Analysis**[a]

| $T_{rct}$ (°C) | $w_p^{VAc}$ | VAc$_{tot}$ | 1B$_2$ | 2B$_4$ | 1A$_3$B$_4$$^+$ | 2B$_5$$^+$ | SCB$_{tot}$ |
|---|---|---|---|---|---|---|---|
| 165 | 0.000 | 0 | 0.9 | 3.3 | 0 | 3.2 | 7.4 |
| 165 | 0.142 | 26 | 1.1 | 3.7 | 0.7 | 3.3 | 9.0 |
| 165 | 0.235 | 48 | 0.7 | 3.4 | 0.7 | 3.3 | 8.3 |
| 165 | 0.386 | 93 | 1.4 | 2.8 | 1.6 | 4.0 | 10.0 |
| 195 | 0.000 | 0 | 1.7 | 4.3 | 0 | 3.7 | 9.7 |
| 200 | 0.140 | 26 | 1.9 | 5.7 | 0.7 | 4.9 | 13.8 |
| 200 | 0.219 | 44 | 1.4 | 4.8 | 1.2 | 4.9 | 12.8 |
| 200 | 0.230 | 46 | 1.5 | 5.3 | 1.2 | 5.1 | 13.4 |
| 200 | 0.381 | 91 | 0.9 | 3.7 | 2.2 | 4.9 | 12.0 |

[a] All numbers (columns 3−8) per 1000 CH$_2$ units.

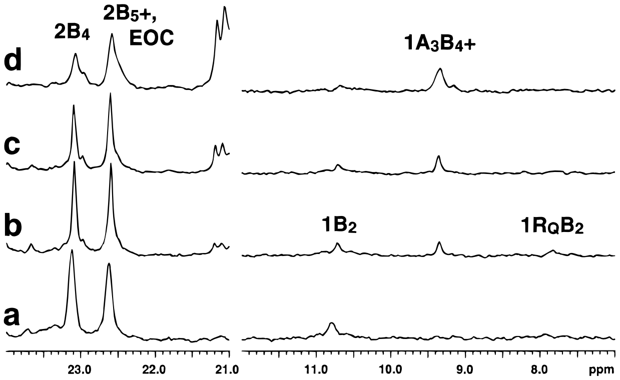

**Figure 10.** Details of 7−12 and 21−24 ppm regions from $^{13}$C NMR spectrum for E/VAc copolymers: (a) ethylene homopolymer (195 °C); (b) 14 wt % VAc (200 °C); (c) 22 wt % VAc (200 °C); (d) 38 wt % VAc (200 °C).

Figure 10 shows that there are now two peaks in the ethyl region—a true ethyl 1B$_2$ peak at 10.8 ppm, and a new peak at 9.5 ppm. This new peak can be assigned to 1A$_3$B$_4$$^+$ and is a strong indication that A$_3$B$_4$ branches are formed by a backbite reaction between an ethylene radical and an ethylene unit in the chain around a VAc unit (see Figure 2b). A 2D NMR experiment (not shown) confirms this assignment. The HSQC−TOCSY technique has previously been used to examine monomer sequencing in E/VAc copolymers,[11] but not SCB structures. We find $^1$H−$^{13}$C correlations connecting the A$_3$B$_4$ methyl carbon at 9.5 ppm to a methylene carbon at 28.2 ppm and then a very weak correlation to a methine carbon at about 72 ppm. There is also a very weak correlation at 28.2 ppm $^{13}$C by 5.0 ppm $^1$H, as expected for the A$_3$B$_4$ structure in E/VAc.

The confirmation of the A$_3$B$_4$ structure refutes the hypothesis of Okada *et al.*,[16] who suggest that the signal at 9.5 ppm can be attributed to the influence of an adjacent VAc unit on a 1B$_2$ signal. We feel the assignment of Okada *et al.* is also improbable, since the backbiting events necessary to form such a structure—a seven-membered ring followed by a second backbiting event—occur too infrequently to result in the branch concentration suggested by the peak intensity. Note also that the size of the A$_3$B$_4$ peak increases with VAc content in the polymer (Figure 10), while the level of "normal" butyl branches decreases (2B$_4$ signal at 23.1 ppm); the sum of the two contributions remains relatively constant. The numbers of amyl$^+$ (2B$_5$$^+$) and 1B$_2$ branches also appear independent of VAc level, as does the total number of SCBs.

The comonomer groups in E/VAc, in contrast to acrylate systems, show no sign of being susceptible to H-abstraction. There are several pieces of evidence supporting this conclusion:

There is no sign of a 1A$_Q$B$_2$ peak in the $^{13}$C NMR spectra (8−12 ppm region).

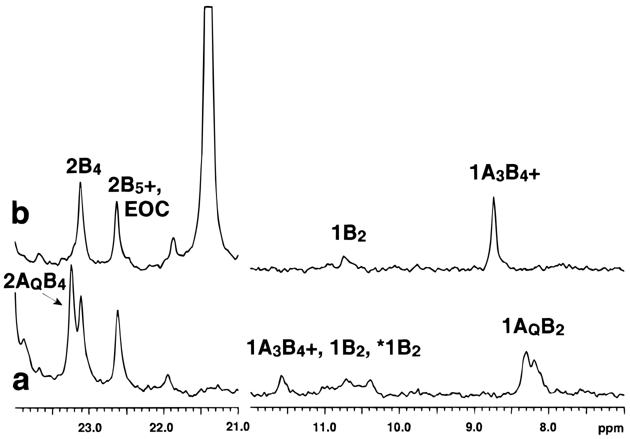

**Figure 11.** Details of 7−12 and 21−24 ppm regions from $^{13}C$ NMR spectrum for (a) E/MMA (methylated from E/MAA) and (b) E/MA (methylated from E/AA).

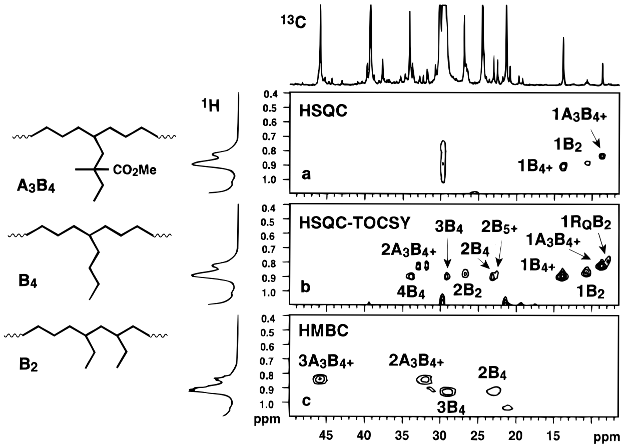

**Figure 12.** 2D 500 MHz NMR correlation spectra for E/MMA copolymer (methylated from E/MAA): (a) HSQC; (b) HSQC−TOCSY; (c) HMBC. See text for further discussion.

> There is no sign of a $2A_QB_4$ peak in the 23 ppm region. (The origin of the side peak on $2B_4$ signal is not presently known. The trends with polymer composition are not consistent with a $2A_QB_4$ structure; although its relative size increases with VAc content in the polymer, the absolute size remains constant, in contrast to the E/nBA resonances at 23−23.5 ppm shown in Figure 6.)
>
> A well-defined $A_3B_4$ peak is observed, in contrast to E/nBA copolymers. For E/nBA polymers, we believe that a large fraction of the $A_3B_4$ structure is converted to an $A_QB_2$ ethyl branch by a second backbiting reaction. This second backbite does not occur in E/VAc, suggesting that the $A_3$ hydrogen is not easily extracted.
>
> A search over the complete NMR spectrum and use of the DEPT pulse sequence technique also showed no evidence of a quaternary C structure that would result from abstraction of the H opposing the acetate group.

Randall *et al.*[21,22] report quaternary carbons of <3% for VAc. However, they admit that their evidence for this structure is weak.[21] We find no evidence that H-abstraction from VAc units occurs in the E/VAc system.

It was reported in the Introduction that literature evidence regarding the presence of acetoxyl-terminated short chain branches is contradictory. Proton NMR spectra for these E/VAc copolymers do show a peak at 4.2 ppm, indicating the presence of a $CH_2$ OAc proton characteristic of acetoxyl-terminated structures.[19] Levels are low, however, in the range of 0.3−0.8% of the total VAc in the polymer. These structures would be formed if VAc radicals participate in short-chain branching mechanisms (Figure 2a), but also may be simply an indication of VAc-ended chains.

**E/AA and E/MAA.** Figure 11 indicates that differences in E/AA and E/MAA polymer microstructure are totally analogous to differences between E/nBA and E/nBMA shown in Figure 6. The $^{13}C$ NMR spectra (7−12 and 21−24 ppm regions) of Figure 11 are for the alkylated E/MMA and E/MA versions of the original acid copolymers. Randall *et al.*[21,22] also report that the E/AA system has a high level of quaternary groups.

2D NMR was used to confirm the identity of the resonances assigned to the $A_3B_4$ structure for a E/MMA (methylated E/MAA) copolymer. In addition to HSQC and HSQC-TOCSY techniques, a gradient HMBC (Heteronuclear Multiple Bond Correlation) experiment was employed for this sample. The HMBC experiment gives correlations between a particular proton and the carbons that are two and three bonds away.[35] Figure 12 shows expanded regions of the HSQC, HSQC-TOCSY, and gradient HMBC experiments. Figure 12a shows the HSQC correlations of the methyl ("1") carbons for $A_3B_4$, $B_2$, and $B_4$+ branches to the methyl protons. (As mentioned in the nBA discussion, $1A_3B_4$ and $1A_3B_5{}^+$ have the same chemical shifts.) Figure 12b shows the HSQC-TOCSY correlations. As for the other copolymer samples, the carbon chemical shifts were adjusted by setting the 2D $^{13}C$ signal for the $A_3B_4$ methyl carbon to 8.7 ppm, the same value as observed in the 1D $^{13}C$ experiment at 120 °C run with $Cr(acac)_3$. A correlation from the methyl proton of $A_3B_4$ to methylenes at 32 and 33 ppm is observed, which are assigned to $2A_3B_4$. The reason for two peaks at 32−33 ppm is not completely understood; it may be due to a seven-membered ring backbiting mechanism and/or EOC structures ($2A_3B_4$ and $2A_3B_5{}^+$), or it may be steric effects. In the HMBC experiment shown in Figure 12c, two correlations from the methyl proton of the $A_3B_4{}^+$ signal are observed. These are assigned to the second (also observed in the HSQC-TOCSY) and third (quaternary) carbon of the $A_3B_4$ branch. Quaternary carbons are not observed in HSQC-TOCSY experiments, due to the nature of the experiment, but are observable in HMBC experiments. This particular quaternary carbon is observed as a result of a 3-bond correlation to the methyl protons, and gives strong support to the proposed $A_3B_4$ branch structure.

## Discussion

A detailed examination of the microstructure of ethylene copolymers by proton, $^{13}C$, and 2D NMR techniques reveals that SCB mechanisms not only occur between ethylene units and ethylene radicals in the system but also involve comonomer units in the chain. Table 4 summarizes the systematic SCB structural differences observed for copolymers of ethylene with acrylates (or acrylic acid), methacrylates (or methacrylic acid), and vinyl acetate. The mechanisms leading to these structures are summarized as Figure 2.

It can be concluded that for the systems examined in this work, most of the intramolecular backbiting originates with ethylene, and not comonomer, radicals. No

**Table 4. SCB Structures in Ethylene Copolymers**[a]

| system | $A_1B_4$ | $A_3B_4$ | $A_QB_4$ and $A_QB_2$ |
|---|---|---|---|
| E/acrylate, E/AA | no | yes (weak) | yes |
| E/methacrylate, E/MAA | no | yes | no |
| E/VAc | yes (weak) | yes | no |

[a] Refer to Figure 2 for structure details.

evidence could be found to support the hypothesis that acrylate or methacrylate radicals participate in backbiting mechanisms. Proton NMR evidence suggests that a small fraction of VAc radicals may backbite along the polymer chain, but the weak signal also may be entirely due to chain-end contributions. Randall *et al.*[21,22] report the presence of a significant number of terminal CN groups in the E/AN polymerization system, suggesting that there are some ethylene-based systems where comonomer radicals do participate in backbiting mechanisms.

Backbiting reactions do occur around comonomer units in the chain. For all of the copolymer systems examined in this work, there is evidence that $A_3B_4$ structures are formed, indicating that the comonomer unit does not prevent the formation of the six-membered ring structure necessary for backbiting. To the best of our knowledge, this is the first time in the literature that such structures have been reported. Note that the secondary carbon radical resulting from this backbite is similar to that obtained in homopolymer backbiting mechanisms.

Finally, there is clear evidence that hydrogens opposing acrylate and acrylic acid side groups are prone to abstraction by backbiting, while those opposing the VAc side group are not. (For methacrylate and MAA systems, of course, the opposing hydrogens do not exist.) This backbiting mechanism leads to the formation of a tertiary carbon radical. A single backbite creates a butyl SCB opposite the acrylate (or acrylic acid) side group, while a double backbite leaves an ethyl SCB. NMR results indicate that a significant fraction of the acrylate (or AA) units are alkylated (10−20%).

The formation of this tertiary radical structure may play an important role in controlling overall reactivity (initiator demand) during production of E/MA, E/nBA, and E/AA copolymers. To understand why, it is necessary to consider what is known about relative radical reactivity. It is generally found that tertiary radicals (formed from methacrylates) have much reduced activity compared to primary (from ethylene) or secondary (from acrylate) radicals.[36−39] Furthermore, experimental studies indicate that increasing the size of the alkyl side chain on a monomer reduces activity even further; the polymerization rate of methyl ethacrylate is an order of magnitude lower than that of methyl methacrylate.[40,41] Thus, the activity of an alkylated acrylate radical (where the alkyl side chain is an ethyl or butyl group) is reduced even further than that of the corresponding methacrylate radical (alkyl side chain is a methyl group).

From the NMR analysis in this work, it is evident that a significant fraction of acrylate (or AA) units in the growing polymer chain are transformed, via backbiting reactions, into much less reactive tertiary radical structures. Thus the ethylene/acrylate polymerization system cannot be thought of (or modeled as) a two-radical two-monomer reaction system. Three radical structures exist in the system, with the tertiary radical present as a significant fraction of the total radical concentration. The presence of the tertiary radical structure significantly reduces the overall reactivity (increases initiator demand) compared to the expected reactivity for a two-radical two-monomer ethylene/acrylate system. Randall *et al.* hypothesize this same effect for the ethylene/acrylonitrile system.[22]

In addition to affecting system reactivity, the level of SCB in comonomer systems can affect physical properties. Saito *et al.*[42] determine that torsional stiffness of E/VAc copolymer is related to SCB level as well as comonomer content. They suggest that it is the sum of SCB and comonomer side groups that is important; polymers of identical composition but differing SCB levels differed in flexibility. Randall *et al.*[21,22] also relate polymer properties (DSC peak melting point) to the total amount of “chain disruptions”—comonomer units and SCB structures—for E/AN copolymer. The presence of SCB structures which contain comonomer units ($A_3B_4$) will reduce the number of effective disruptions.

Finally, we note that the susceptibility of comonomer units in the polymer chain to hydrogen abstraction by a SCB mechanism should be related to the frequency of long-chain branching events (intermolecular transfer to polymer) in the system. The SCB results also give insight into the debate as to whether LCBs from comonomer units are formed by H-abstraction from the main polymer backbone or from the acrylate or acetate side groups. Lovell *et al.*[32] report significant LCB from the main polymer backbone for nBA homopolymer, as do Wolk and Eisenhart;[43] the latter authors also show that branching from the ester group is not detectable. These findings are in accord with the present NMR study—the hydrogen opposite the acrylate group on the main polymer backbone is very susceptible to abstraction. Indeed, 10−15% of comonomer units in E/nBA copolymer are found to be quaternary, much higher than the 2−4% SCB levels found per ethylene in homopolymer.

The locus of LCB in VAc systems remains a matter of debate. Sequential saponification and reacetylation is often used to determine the amount of branching through the acetate group. Results, however, vary widely; for VAc homopolymer, reports of the fraction of branch points that originate from the acetate group vary from less than 50% to greater than 95%.[44] Studies of E/VAc copolymers conclude that the majority of branching from VAc units occurs from the acetate group,[14,45] with perhaps some branching from the main polymer chain.[46] In this work, no evidence of quaternary carbons was found, suggesting that abstraction of a backbone hydrogen from VAc is not favored and indirectly supporting the conclusion that long-chain branching from VAc units is more likely to occur from the acetate group.

## Conclusions

A systematic study of ethylene copolymers reveals that comonomer units play an active role in backbiting mechanisms. Short-chain branches originating from comonomer units ($A_QB_4$, $A_QB_2$) and containing comonomer units ($A_3B_4$) have been identified by NMR techniques, with the type and frequency of branches a function of polymerization temperature, comonomer content in the polymer, and type of comonomer. No evidence (with the possible exception of E/VAc copolymer) of branches terminated by a comonomer unit ($A_1B_4$) could be found. A consistent picture of short-chain branching mechanisms in ethylene copolymer systems has emerged, providing insights into important reaction issues such as relative reactivity and long-chain branching.

**Acknowledgment.** We would like to thank K. D. Raffell for excellent technical assistance and D. Brown for his helpful advice on the HSQC−TOCSY and hsmqc pulse sequences. We also thank D. R. Marshall, J. W. Paul, C.-H. Hsu, and M. E. Wagman for providing copolymer samples. Finally, we thank B. Adams and Varian Instrument Co. for use of their 500 MHz spectrometer for the E/MMA 2D experiments.

## References and Notes

(1) Roedel, M. J. *J. Am. Chem. Soc.* **1953**, *75*, 6110−6133.
(2) *Encyclopedia of Polymer Science and Technology*, 2nd ed.; John Wiley and Sons: New York, 1989; Vol. 6, pp 383−429.
(3) Willbourn, A. H. *J. Polym. Sci.* **1959**, *34*, 569.
(4) Usami, T.; Takayama, S. *Macromolecules* **1984**, *17*, 1756.
(5) Ehrlich, P.; Mortimer, G. A. *Adv. Polym. Sci.* **1970**, *7*, 386.
(6) Axelson, D. E.; Levy, G. C.; Mandelkern, L. *Macromolecules* **1979**, *12*, 41.
(7) Prasad, J. V.; Rao, P. V. C.; Garg, V. N. *Eur. Polym. J.* **1991**, *27*, 251.
(8) Wu, T. K.; Ovenall, D. W.; Reddy, G. S. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 901.
(9) Ibrahim, B.; Katritzky, A. R.; Smith, A.; Weiss, D. E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1537.
(10) Sung, H. N.; Noggle, J. H. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1593.
(11) Beshah, K. *Macromolecules* **1993**, *25*, 5597.
(12) Moritani, T.; Iwasaki, H. *Macromolecules* **1978**, *11*, 1251.
(13) Amiya, S.; Iwasaki, H.; Fujiwara, Y. *Nippon K. K.* **1977**, *11*, 1698.
(14) Wagner, T.; Schlothauer, K.; Schneider, H. *Plaste Kautsch.* **1982**, *11*, 637.
(15) Grenier-Loustalot, M.-F. *Eur. Polym. J.* **1985**, *21*, 361.
(16) Okada, T.; Hashimoto, K.; Ikushige, T. *Chem. Soc. Jpn. J.* **1980**, *1*, 74.
(17) Bugada, D. C.; Rudin, A. *Eur. Polym. J.* **1992**, *28*, 219.
(18) Viswanadhan, V. N.; Mattice, W. L. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1957.
(19) Wisotsky, M. J.; Kober, A. E.; Zlochower, I. A. *J. Appl. Polym. Sci.* **1971**, *15*, 1737.
(20) Bruch, M. D.; Payne, W. G. *Macromolecules* **1986**, *19*, 2712.
(21) Randall, J. C.; Ruff, C. J.; Kelchtermans, M. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 543.
(22) Randall, J. C.; Ruff, C. J.; Kelchtermans, M.; Gregory, B. H. *Macromolecules* **1992**, *25*, 2624.
(23) Bodenhausen, G.; Ruben, D. *J. Chem. Phys. Lett.* **1980**, *69*, 185.
(24) Braunschweiler, L.; Ernst, R. R. *J. Magn. Reson.* **1983**, *53*, 521.
(25) Davis, D. G.; Bax, A. *J. Am. Chem. Soc.* **1985**, *107*, 2820.
(26) Brown, D., personal communication, 1995.
(27) Luft, G.; Kämpf, R.; Seidl, H. *Angew. Makromol. Chem.* **1982**, *108*, 203.
(28) Mattice, W. L.; Stehling, C. F. *Macromolecules* **1981**, *14*, 1479.
(29) Mattice, W. L. *Macromolecules* **1983**, *16*, 487.
(30) Bowmer, T. N.; O'Donnell, J. H. *Polymer* **1977**, *18*, 1032.
(31) Von Dohlen, W. C.; Wilson, T. P. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2511.
(32) Lovell, P. A.; Shah, T. H.; Heatley, F. *Polym. Commun.* **1991**, *32*, 98.
(33) Galya, L. G.; McCord, E. F.; Adamsons, K. *Int. J. Polym. Anal. Char.* **1996**, *2*, 293.
(34) Wehrli, F. W.; Marchand, A. P.; Wehrli, S. *Interpretation of Carbon-13 NMR Spectra*, 2nd ed.; John Wiley and Sons: New York; 1983. p 52.
(35) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.
(36) Bamford, C. H. The Synthesis, Characterization, Reactions & Applications of Polymers. *Comprehensive Polymer Science: Chain Polymerization I*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, England, 1989; Vol. 3, Chapter 17.
(37) Hutchinson, R. A.; Paquet, D. A., Jr.; McMinn, J. H.; Fuller, R. E. *Macromolecules* **1995**, *28*, 4023.
(38) Beuermann, S.; Paquet, D. A., Jr.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206.
(39) Bergert, U.; Buback, M.; Heyne, J. *Macromol. Rapid Commun.* **1995**, *16*, 275.
(40) Penelle, J.; Collot, J.; Rufflard, G. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 2407.
(41) Bergert, U. Ph.D. Thesis, Universität Göttingen, Cuvillier Verlag, Göttingen, Germany, 1994.
(42) Saito, M.; Tada, H.; Kosaka, Y. *J. Polym. Sci., Part A-1* **1970**, *8*, 2555.
(43) Wolk, S. K.; Eisenhart, E. *Macromolecules* **1993**, *26*, 1086.
(44) Lindemann, M. K. The Mechanism of Vinyl Acetate Polymerization. In *Vinyl Polymerization;* Ham, G. E., Ed.; Marcel Dekker, Inc.: New York, 1967; Vol. 1, Part 1.
(45) Brauer, E.; Wiegleb, H.; Gebauer, E. *Plaste Kautsch.* **1985**, *14*, 444.
(46) Roland, J. R.; Richards, L. M. *J. Polym. Sci.* **1952**, *IX*, 61.

MA9606871