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Carbon-13 NMR Characterization of Ethylene–Acrylonitrile Copolymers Prepared by High-Pressure Free-Radical Polymerizations

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ABSTRACT: A series of copolymers of ethylene and acrylonitrile, produced by high-pressure free-radical polymerization, were recovered from a reactor in low yields. The copolymers differed by melting points and profiles of the melting point distributions. These were characterized utilizing carbon-13 NMR for the structures and amounts of incorporated acrylonitrile (AN) repeat units. The carbon-13 NMR spectra were consistent with five principal modes of acrylonitrile incorporation. Each of the five different repeat unit structures contained only isolated acrylonitrile units, with only one being a linear –E–AN–E– structural sequence. It represented approximately 65% of the acrylonitrile incorporation. The remaining structures were rationalized in a common manner by considering variations in the Roedel free-radical "back-biting" mechanism. Similar distributions of these five structures were observed independently of the total level of acrylonitrile. Interestingly, evidence for free-radical chain-transfer reactions involving terminal acrylonitrile units indicated that such reactions occurred to an extent of only about 6–7%. In the residues examined, there were essentially no consecutive sequences of acrylonitrile units, and polyacrylonitrile homopolymeric sequences were detected at only about 1%.

Introduction

A series of five copolymers, differing only by acrylonitrile levels, were prepared by free-radical polymerization of ethylene and acrylonitrile (AN) in a high-pressure reactor.[1] Soluble polymeric materials, extracted from the reactor, were obtained in very low yields with molecular weights that decreased with increasing acrylonitrile content. These residues from five different E/AN polymerization compositions were examined structurally to determine if copolymerization had occurred. Published kinetic data for the polymerization of ethylene and acrylonitrile indicated that the relative acrylonitrile reactivity would be low, which suggests that homopolymerization of acrylonitrile would be favored.[2] Differential scanning calorimetry (DSC) of the five recovered polymeric materials revealed that an increasing acrylonitrile incorporation led to a corresponding broader melting range accompanied by a general reduction in melting points and crystallinity. The peak melting points centered from approximately 108 to 67 °C as the acrylonitrile content increased from approximately 2 to near 11 mol %. There was only a general correlation between incorporated acrylonitrile content and melting point behavior. Further characterization was needed to resolve detailed differences between melting behavior and mole percent acrylonitrile determined from carbon-13 NMR. Certainly aliphatic branching could contribute to a reduction in melting behavior as well as incorporation of acrylonitrile. Also to be established were the arrangements of the acrylonitrile units in the copolymer chains. Are they present as consecutive sequences of AN units, either in short sequences or as block copolymer segments, or could they be present in a more random manner? Again, from kinetic data, consecutive AN units would be anticipated and could also lead to observed differences between melting points and acrylonitrile contents.

The techniques that have the capability to yield this desired structural information are carbon-13 and proton NMR. There is a problem in obtaining reference information for an NMR study because there are no published carbon-13 or proton spectral assignments available for E/AN copolymers. The only published complete carbon-13 NMR spectral assignments are for the ethylene homopolymers prepared in a high-pressure reactor[3] and for acrylonitrile homopolymers[4] and uninterrupted acrylonitrile sequences.[5] Literature proton polyacrylonitrile spectra[6] offer confirming evidence for identifying the presence of continuous AN sequences, but no reference information is available for identifying randomly incorporated AN sequences.

The pulse techniques, APT and DEPT, were utilized to identify carbon types that would lead to tentative resonance assignments in the carbon-13 NMR spectra. Fortunately, the concentration of incorporated AN units varied sufficiently from sample to allow patterns of "new" resonances to be easily recognized. These "new" resonances had not previously observed in the NMR spectra of the corresponding ethylene and acrylonitrile homopolymers. Consequently, these various "new" patterns could be associated with different modes of AN incorporation.

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Table I
Experimental Conditions Concerning Preparation and Observed Melting Points of a Series of Ethylene–Acrylonitrile Copolymers Prepared by High-Pressure Free-Radical Polymerization

sample	mol % AN[a]	melt index, (d*g*/*M*)	peak mp, °C	reactor conditions press., bar	reactor conditions temp, °C
1	1.6	0.7	107.8	1900	207
2	2.5	0.2	107.3	1900	189
3	7.0	2.2	95.7	1500	199
4	7.5	11.0	66.8	1500	176
5	10.7	16.9	90.5	1300	220

[a] Determined from carbon-13 NMR analyses of the copolymers.

The chemical shifts and relative intensities of resonances within a given pattern gave sufficient structural information for a generic type of structure to be identified. These structures could be made more specific after examining the various free-radical pathways that could lead to different modes of acrylonitrile incorporation. When this process was completed, five different modes of acrylonitrile incorporation were tentatively identified.

Although yields were very low and only soluble polymeric material was examined, it was significant to note from the standpoint of spectral assignments that uninterrupted AN sequences were observed at a low extent. Only about 1% of the copolymer product structures could be described as consisting of continuous AN sequences. Alkyl branches, formed through normal back-biting chemistry during ethylene polymerization in high-pressure reactors, appeared to be reduced somewhat from the amount observed in typical low-density polyethylenes.[7-9] The majority of side-chain branches were associated in some manner with acrylonitrile repeat units. The basic mode of AN incorporation was in -E-AN-E- sequences, although only about 65% of these -E-AN-E- sequences involved a linear arrangement of ethylene–acrylonitrile–ethylene units. A good correlation was observed between the DSC melting behavior and the complete NMR composition data, when it included aliphatic branching in addition to acrylonitrile contents.

An identification of the various free-radical "back-biting" pathways was an essential step to obtaining a complete interpretation of the NMR data. Overall, the study may be useful from the viewpoint that it may provide a framework for more complete spectral interpretations of the branching and modes of comonomer incorporation in other ethylene copolymers produced in high-pressure processes. A brief discussion of ethylene–vinyl acetate, ethylene–acrylic acid, and ethylene–methyl acrylate copolymers is given near the end of the report.

Experimental Section

Information concerning the preparation and melting points of the various E/AN copolymers is given in Table I. The DSC melting curves of each of these polymeric products are reproduced in Figure 1. Each sample gave a broad melting point distribution. The "peak melting points" given in Table I were taken from the highest point of the DSC melting point curves as shown by the lines in Figure 1. The relative molecular weights can be inferred by the melt index measurements in Table I. The melt indices increase with increasing acrylonitrile incorporation. The mole percent acrylonitrile, based on carbon-13 NMR analyses, is also given in Table I for each sample.

Carbon-13 and proton NMR spectra were obtained on a Varian XL-200 NMR spectrometer. Carbon-13 NMR acquisition conditions were pulse angle, 90°; pulse delay, 10 s; acquisition time, 1 s; sweep width, 8000 Hz; and the number of fid's (free induction decay signals) typically collected per sample was around 5000.

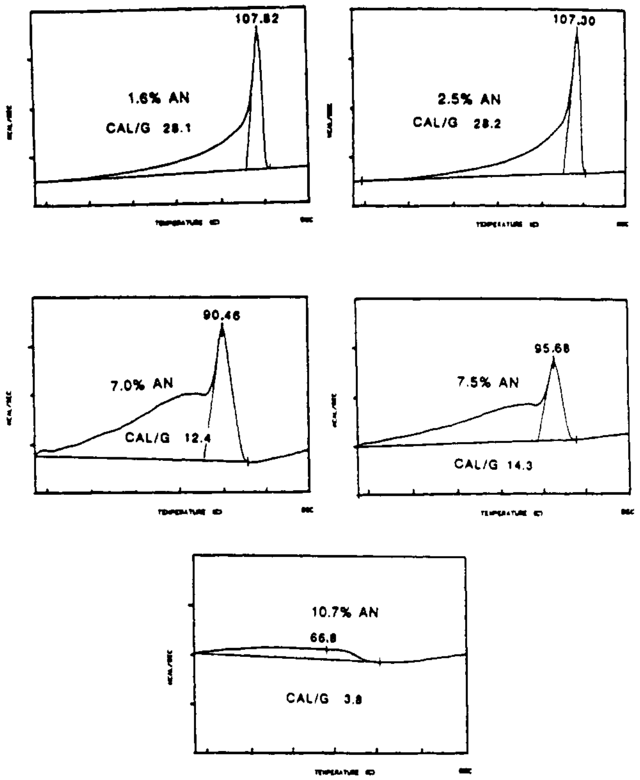


Figure 1. Differential scanning calorimetry thermograms showing the melting behavior of a series of ethylene–acrylonitrile copolymers differing by AN content.

The NMR data for one of the samples were collected with pulse delays of 10 and 20 s. A noticeable change occurred for the nitrile carbon resonances, which increased in intensity with a 20-s pulse delay. The amount and distribution of acrylonitrile units, determined by the method presented in this study, were the same for both the 10- and 20-s pulse delay experiments. A 10-s pulse delay will be adequate in carbon-13 NMR analyses of low-density polyethylene homopolymers and copolymers as long as terminal carbons from branches or chain ends are not utilized in the quantitative analyses. Broad-band proton noise decoupling was utilized during data acquisition. Each sample was dissolved at approximately 15% by weight in tetrachloroethane-d_2, and spectra were obtained nominally at 125 °C. The solvent also served as a source of deuterium for an internal lock signal.

The pulse sequences, APT (attached proton test) and DEPT (distortionless enhanced polarization transfer), were used to identify each type of resonance produced in the carbon-13 NMR spectra. In spectra taken with the DEPT technique, the methyl and methine carbon resonances are 180° out of phase (up) with respect to the methylene carbon resonances (down). The quaternary carbon resonances are nulled by this technique. The APT technique was used specifically to observe quaternary carbon resonances by obtaining spectra where all resonances from carbons having attached protons were nulled. These techniques allowed every type of carbon resonance in the spectra of the various E/AN copolymers to be identified according to whether they originated from methyl, methylene, methine, or quaternary carbons.

Carbon-13 NMR area measurements were determined by integration of specifically selected spectral regions as will be seen later. Gated decoupling experiments were performed to detect any possible differences among nuclear Overhauser effect contributions. Similar quantitative results were obtained with and without gated decoupling. Also, the relative distributions of structures determined by spectral integration were the same whether gated decoupling was utilized or not. From these results, it was concluded that similar nuclear Overhauser effects existed throughout the spectral regions used for quantitative measurements.

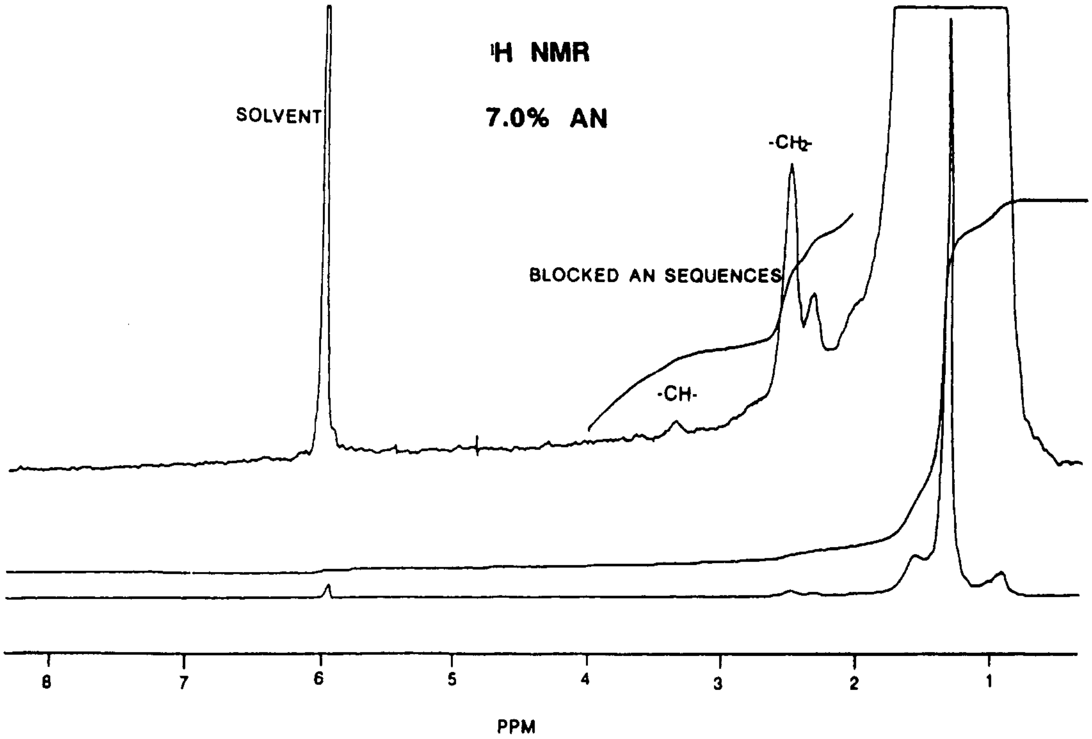


Figure 2. Proton NMR spectrum at 200 MHz of an ethylene–acrylonitrile copolymer containing 7.0 mol % acrylonitrile.

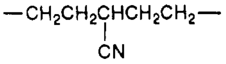
Table II
Percent Uninterrupted Acrylonitrile Sequences in Copolymers of Ethylene and Acrylonitrile Prepared by High-Pressure Free-Radical Polymerization

sample	mol % AN (by ^{13}C NMR)	mol % consecutive AN sequences (by ^1H NMR)
1	1.6	none detected
2	2.5	0.3
3	7.0	1.0
4	7.5	0.5
5	10.7	0.6

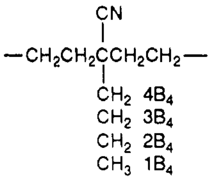
Results and Discussion

Proton NMR spectra of the series of ethylene–acrylonitrile copolymers were useful for detecting the presence of any continuous sequences of acrylonitrile repeat units. Polyacrylonitrile produces a methine resonance at 3.35 ppm and a methylene resonance at 2.3–2.6 ppm.[6] A proton NMR spectrum of the 7.0 mol % AN copolymer is reproduced in Figure 2. The proton NMR spectra of these copolymers showed only a weak resonance at 3.35 ppm that could be used to determine the content of continuous acrylonitrile sequences. The 3.35 ppm resonance appeared as a shoulder on a much stronger resonance occurring to the high-field side. The remaining proton resonances occurred between 0.5 and 2 ppm and, consequently, offered very little definitive structural information regarding other ways acrylonitrile was incorporated. The mole percent continuous AN sequences, as determined from proton NMR, are given in Table II for each of the copolymers. As can be noted in Table II, there appears to be no correlation between the mole percent of continuous acrylonitrile sequences and the total acrylonitrile content in the copolymer. This result suggests that the continuous acrylonitrile sequences may result from polyacrylonitrile produced as a byproduct.

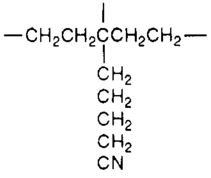
Carbon-13 NMR spectra of three of the ethylene–acrylonitrile copolymers are given in Figure 3. To permit a closer inspection, an expanded spectrum of the 7.0 % AN copolymer is shown in Figure 4. These spectra were selected because they represented the extremes and mid range of the incorporated acrylonitrile levels. A line listing of assignments determined either from the various pulse techniques or by comparison with known assignments from low-density polyethylenes is given in Table III. They are grouped as regions I–XIV according to particular structural characteristics and the ease with which the spectral regions could be measured quantitatively. Patterns of resonances, which are identified as A–E in Figures 3 and 4, could be grouped according to relative intensity relationships. These led to an identification of the following proposed structures, which are labeled according to the corresponding resonance pattern, A–E, below:


$-CH_2CH_2\underset{CN}{CH}CH_2CH_2-$

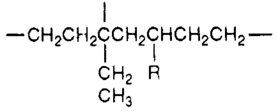
A


$-CH_2CH_2\overset{CN}{\underset{\begin{array}{l}CH_2\ 4B_4\\CH_2\ 3B_4\\CH_2\ 2B_4\\CH_3\ 1B_4\end{array}}{C}}CH_2CH_2-$

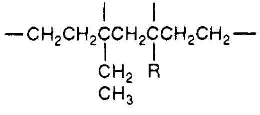
B


$-CH_2CH_2\overset{CN}{\underset{\begin{array}{c}CH_2\\CH_2\\CH_2\\CH_2\\CN\end{array}}{C}}CH_2CH_2-$

C


$-CH_2CH_2\overset{CN}{\underset{\begin{array}{c}CH_2\\CH_3\end{array}}{C}}CH_2\underset{R}{CH}CH_2CH_2-$

D


$-CH_2CH_2\overset{CN}{\underset{\begin{array}{c}CH_2\\CH_3\end{array}}{C}}CH_2\overset{R}{\underset{R}{C}}CH_2CH_2-$

E

It can be clearly seen in Figure 3 that the spectral patterns for A–E increase in intensity as the acrylonitrile content in the copolymers increases. The methyl resonance near 14 ppm next to the highest field "B" resonance can be

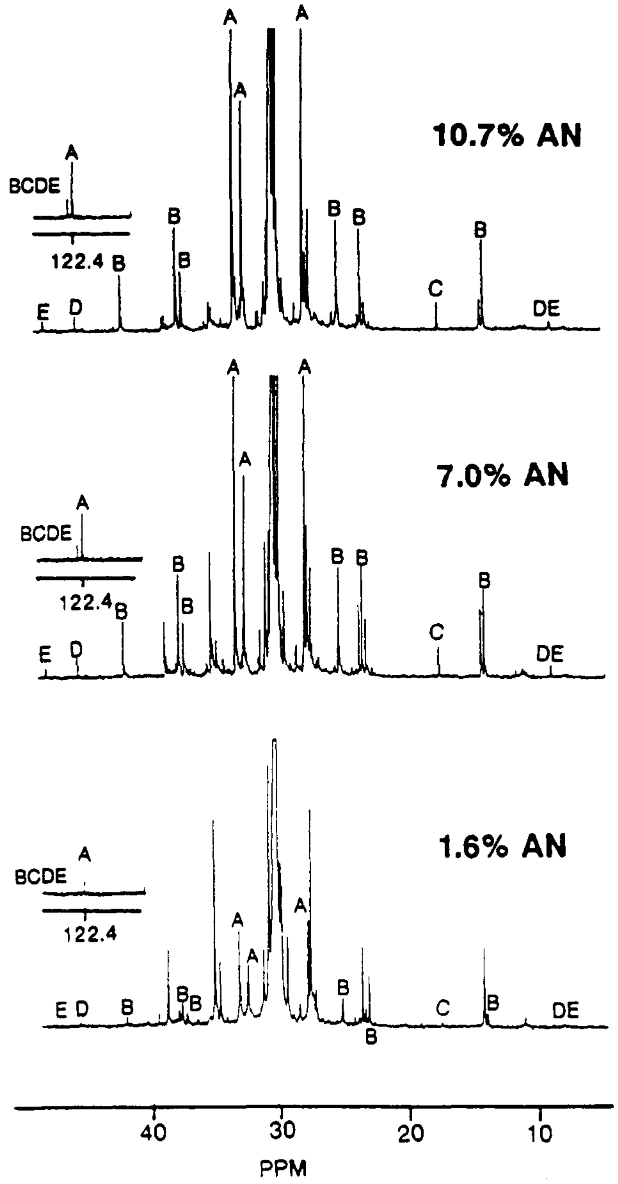
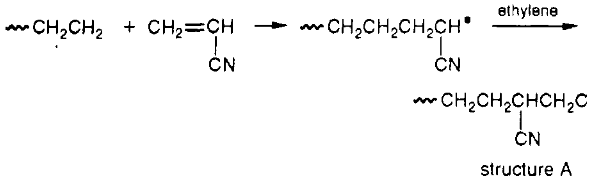


Figure 3. Carbon-13 NMR spectra of a series of ethylene–acrylonitrile copolymers differing in acrylonitrile content.

used as a reference intensity for comparison since it originates from branches not associated with acrylonitrile incorporation. Those resonances typically observed in carbon-13 NMR spectra of low-density polyethylenes are identified as "LDPE". In the following paragraphs, the reasons for selecting specific regions for quantitative measurements and the analyses leading to the various structural identifications are discussed in detail.

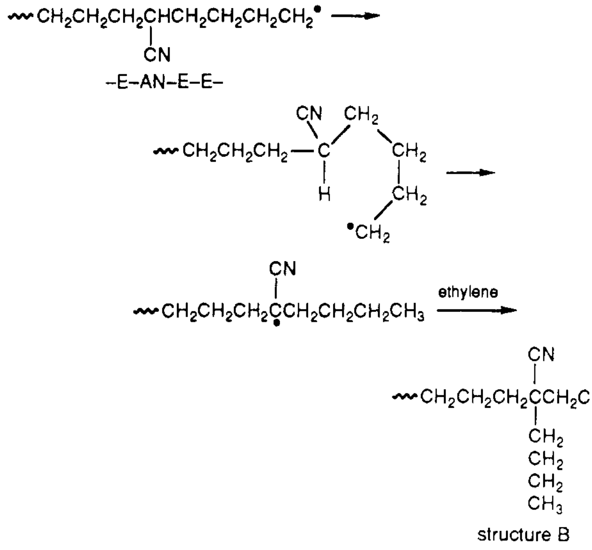
In the upcoming formulas and in Table III, Greek symbols are used to designate the location of methylene carbons along the polymer chain backbone. The "distance" in carbon atoms from a methylene carbon of interest to the nearest branched carbon in either direction is indicated by a pair of Greek letters.[10] An $\alpha\alpha$ means that the methylene carbon has methine carbons for both immediate neighbors. An $\alpha\gamma$ means that the branch in one direction is on an adjacent carbon while the branch in the opposite direction is three carbons removed. An $\alpha\delta^+$ indicates a methine carbon is an immediate neighbor in one direction while the second methine carbon in the opposite direction is four or more carbons removed, and so forth. Branch carbons are identified by an "nB$_i$". The subscript, "i", indicates the length of the branch while the numerical prefix, "n", indicates the position in the branch. The methyl end of the branch is number "1".

Structure "A" is produced by a linear addition of an acrylonitrile unit to the free-radical end of a growing polyethylene chain, that is



The methine resonance for structure A uniquely occurs at 32.12 ppm, with the $\alpha\delta^+$ resonance being observed at 32.82 ppm and the $\beta\delta^+$ at 27.53 ppm. Neither of these resonances is found in carbon-13 NMR spectra of conventional low-density polyethylene homopolymers. The resonance at 32.12 ppm was unequivocally identified as arising from a methine carbon by the DEPT technique as shown in Figures 5 and 6. This location is somewhat unusual for a methine carbon resonance and is a result of an anticipated upfield shielding effect by the nitrile group.

Each of the structures B–E can be rationalized through a series of Roedel back-biting steps involving six-membered cyclic transition states containing five carbon atoms. Structure B is produced after a normal insertion of acrylonitrile into the growing polyethylene chain followed by a single back-biting step after two ethylene additions which permit a six-membered cyclic transition state:



A number of resonances are available that lead to a positive identification of structure B. A quaternary carbon resonance was found at 41.37 ppm by the attached proton test as shown in Figure 7. The backbone resonances, $\alpha\delta^+$ and $\beta\delta^+$, are located at 37.17 and 24.89 ppm, respectively. These intensities should be the same and at twice the level of that for the side-chain butyl group resonances. Of importance is the chemical shift of $4B_4$ of the butyl group bonded to a quaternary carbon that also bears a nitrile group. It should have a chemical shift similar to $\alpha\delta^+$ and at one-half the intensity. This $4B_4$ resonance is easily identified at 36.79 ppm. Resonances for $1B_4$ and $2B_4$ are located at 13.93 and 23.16 ppm, respectively. Both show upfield shifts from the corresponding carbons in the LDPE butyl branch. The $3B_4$ carbon resonance from the butyl group bonded to the quaternary carbon apparently overlaps with the strong 30 ppm $\delta^+\delta^+$ resonance as does the corresponding $3B_4$ for butyl branches in low-density

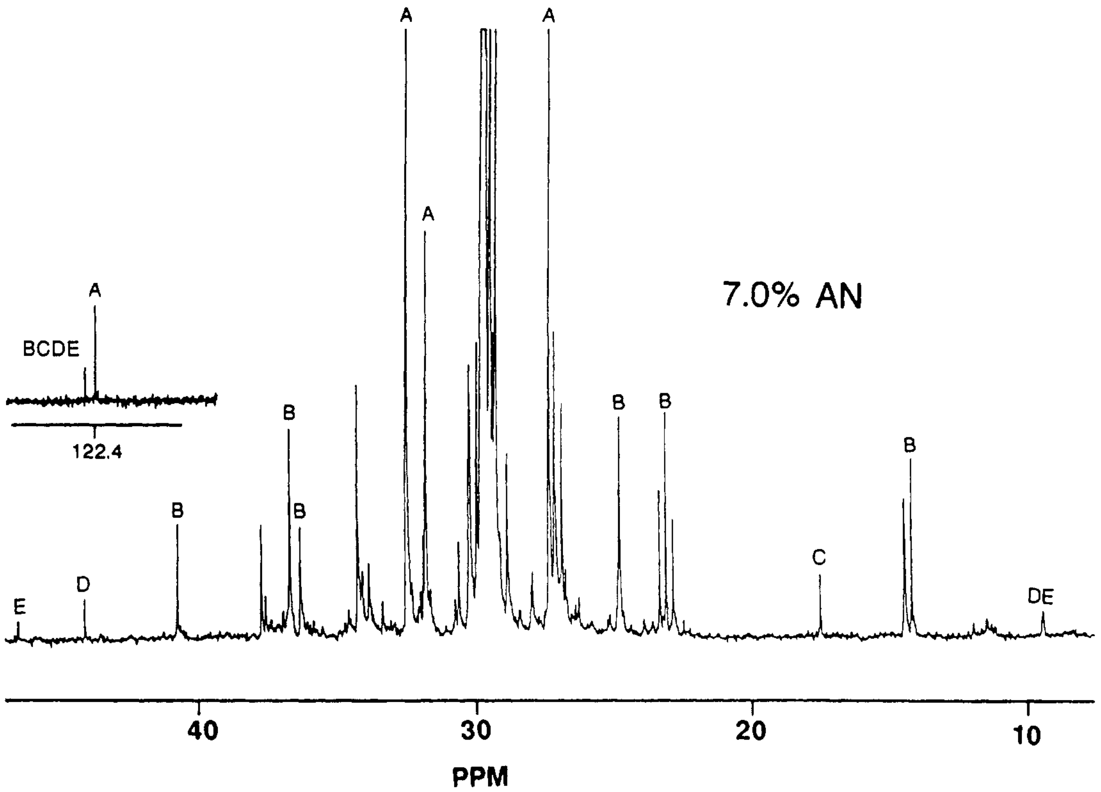


Figure 4. Carbon-13 NMR spectrum of an ethylene–acrylonitrile copolymer containing 7.0 mol % acrylonitrile.

Table III
Line Listings for Carbon-13 NMR Resonances in Ethylene–Acrylonitrile Copolymers

region	range, ppm	specific key resonances, ppm	assignments	pattern
I	121–125	124.30	CN on a quaternary C	BCDE
		122.41	CN on a tertiary C	A
		118.6	CN on a secondary C	C
II	44–48	47.22	$\alpha\alpha$ CH_2 between quaternary C's	E
		44.80	$\alpha\alpha$ CH_2 between a methine and a quaternary C	D
III	41–42	41.37	quaternary C bonded to a nitrile group	B
IV	36–39	38.25	methine carbon	LDPE
		37.17	CH_2 $\alpha\delta^+$ to a quaternary C(CN)(butyl)(R)	B
		36.79	$4B_4$ CH_2 (butyl on a quaternary carbon)	B
V	33–35	34.65	$\alpha\delta^+$ CH_2 to a butyl group	LDPE
		34.24	$4B_4$ CH_2	LDPE
		33.73	? CH_2	?
VI	32–33	32.82	CH_2 ($\alpha\delta^+$ to CHCN)	A
		32.21	$3B_6$ CH_2 (or 3s[a])	LDPE
		32.12	methine having a CN group	A
VII	29–31	30.48	$\gamma\delta^+$ CH_2	LDPE
		29.98	$\delta^+\delta^+$ CH_2	LDPE
		29.08	? CH_2	LDPE
VIII	26–28	27.53	CH_2 $\beta\delta^+$ to CHCN	A
		27.33	CH_2 $\beta\delta^+$ to B_2^+	LDPE
		27.06	? CH_2	?
IX	24–25	24.89	CH_2 $\beta\delta^+$ to a quaternary C(CN)(butyl)(R)	B
X	22–24	23.40	$2B_4$ CH_2	LDPE
		23.16	$2B_4$ CH_2 from a butyl group on a quaternary C	B
		22.86	$2B_5^+$ (2s[a])	LDPE
XI	17–18	17.37	CH_2 α to terminal CN	C
XII	13–15	14.21	$1B_4$ CH_3 (and 1s[a])	LDPE
		13.93	$1B_4$ CH_3 from butyl on a quaternary C	B
XIII	10–12	11.13	$1B_2$ CH_3 from 1,3-diethyl branches	LDPE
		10.83	$1B_2$ CH_3 from a sequence of branches	LDPE
XIV	8–9	8.9	$1B_2$ CH_3 on quaternary C(CN)	DE
		8.2	$1B_2$ CH_3 on quaternary C	LDPE

[a] 1s, 2s, and 3s designate the first three carbons, respectively, of a normal aliphatic polymer chain end group.

polyethylenes. As can be seen in Figure 5, the peak heights for the $1B_4$ and $2B_4$ resonaces are close in intensity to the peak heights observed for the $\alpha\delta^+$ and $\beta\delta^+$ resonances, when, in fact, a 2:1 relationship is expected. This observation is somewhat deceptive because the side-chain resonances have more narrow line widths than the main-chain resonances. The relative areas for these backbone versus side-chain resonances show the 2:1 relationship, as expected. In most cases, either line widths or the relative areas can be used to distinguish backbone carbon reso-

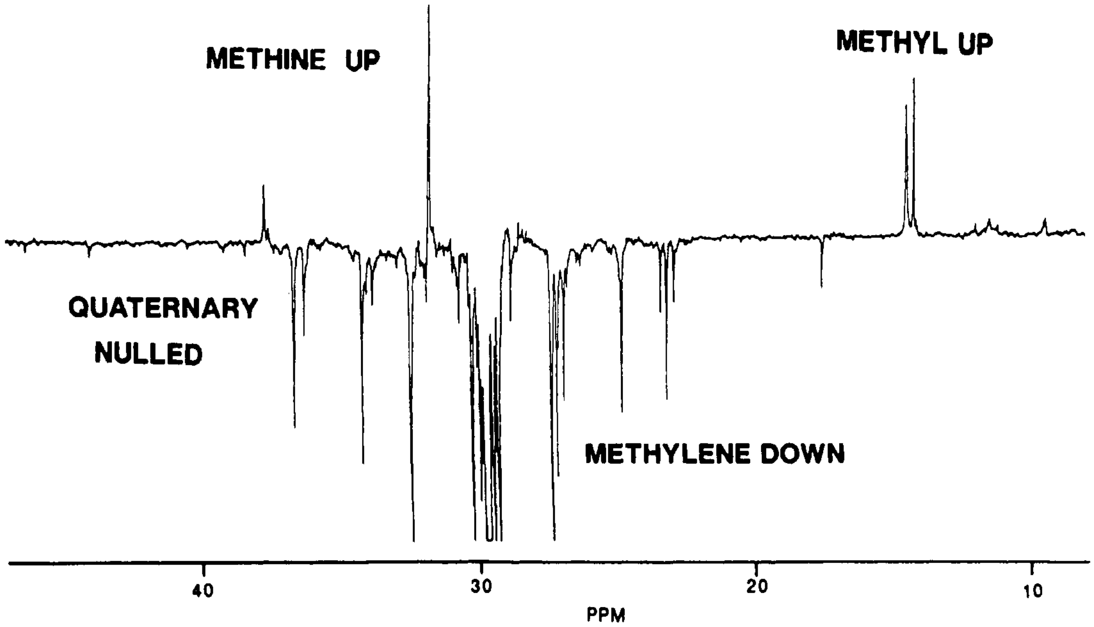
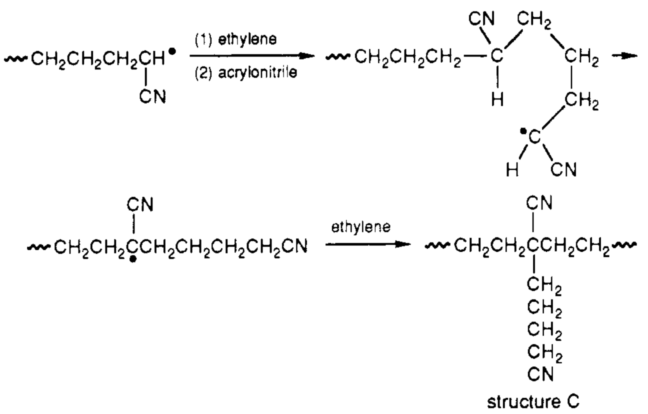


Figure 5. DEPT experiment for the 7.0 mol % E/AN copolymer. Methine and methyl resonances are "up" while methylene resonances are "down". Quaternary resonances are nulled.

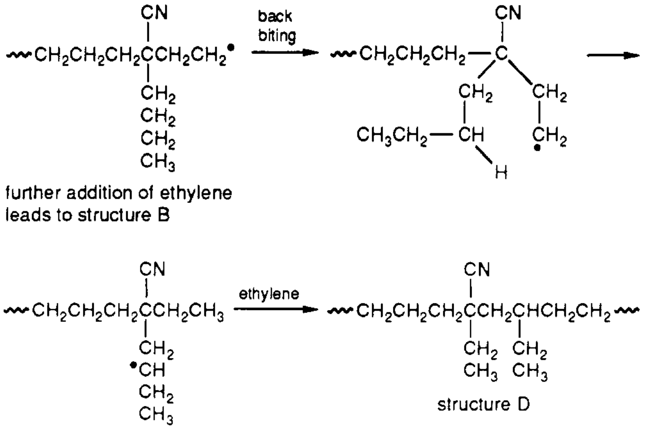
nances from side-chain carbon resonances. The peak height relationship for $\alpha\delta^+$:$4B_4$ is 2:1 because these resonances have similar line widths since the $4B_4$ carbon is bonded directly to the main chain and experiences similar molecular motions. Thus the various carbon-13 NMR experiments provide abundant and internally consistent spectral information that allows the identification of structure B.

Structure C is produced by an intramolecular chain-transfer reaction whenever the acrylonitrile unit is the terminal unit of the growing polymer chain. Once again, a similar cyclic transition state containing five carbons during a back-biting step leads to the proposed product. It is likely, although unproven, that this back-biting step involves a second nitrile carbon at the transfer site to provide a driving force for the back-biting chemistry.



The methylene carbons α to terminal CN groups give a resonance at 17.37 ppm. This position was confirmed by comparison to similar structural moieties in closely related model compounds.[11] The resonance for carbons β to the CN group in the $CH_2CH_2CH_2CH_2CN$ side chain could not be located as a separate and easily identified spectral line. It apparently overlaps with other resonances from related types of branches. The carbons γ and δ to the nitrile group are expected to overlap with the resonances for $4B_4$ and $3B_4$ from the corresponding type of butyl branch in structure B. The identification of structure C is therefore based only on a single, but significant observation because the $CH_2CH_2CH_2CN$ moiety was identified. This particular structural species is a unique result from either a Roedel intramolecular chain-transfer reaction or a corresponding intermolecular chain-transfer reaction involving a terminal acrylonitrile unit. The branch structure in C will have a number of methylene carbons that relates to the size of the cyclic transition state during the back-biting step. Structure C is depicted as having four such methylene carbons between the quaternary carbon and the terminal CN group because a cyclic intermediate containing five carbons is consistent with the chemistry producing the remainder of the structural moieties involving acrylonitrile units. The next higher possibility would have six methylene carbons and require a seven carbon atom cyclic transition state. Intermolecular chain transfer involving a terminal acrylonitrile unit, of course, is also plausible and the presence of a CH_2CN moiety from both sources must be considered. The identification of a chain-transfer reaction involving a terminal acrylonitrile unit is the important conclusion.

Structure D arises from the same precursor that leads to structure B but requires a second back-biting step, once again, with a cyclic transition state containing five carbon atoms. The following free-radical back-biting scheme leads to structure D:



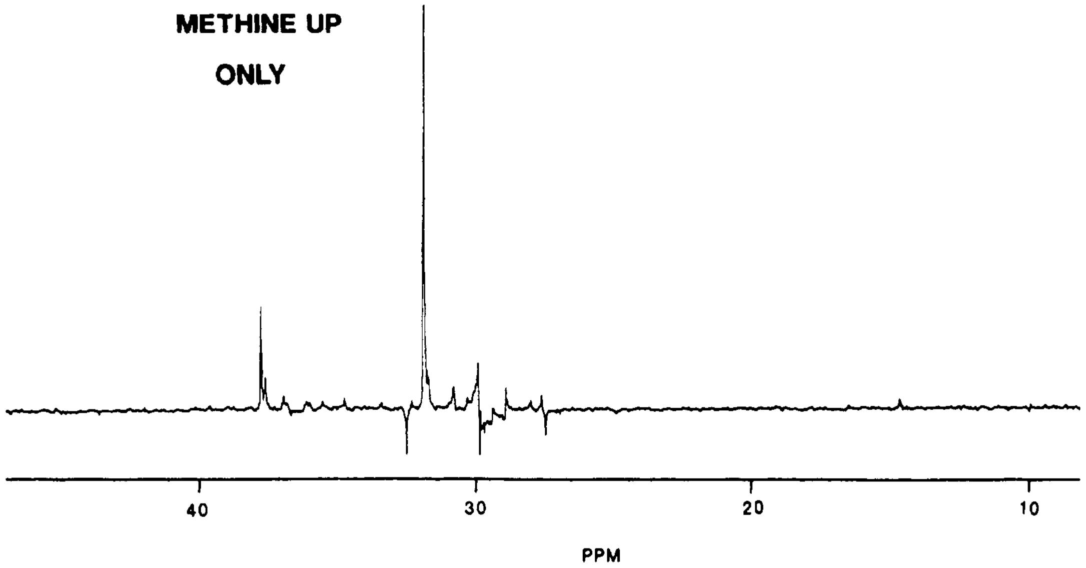
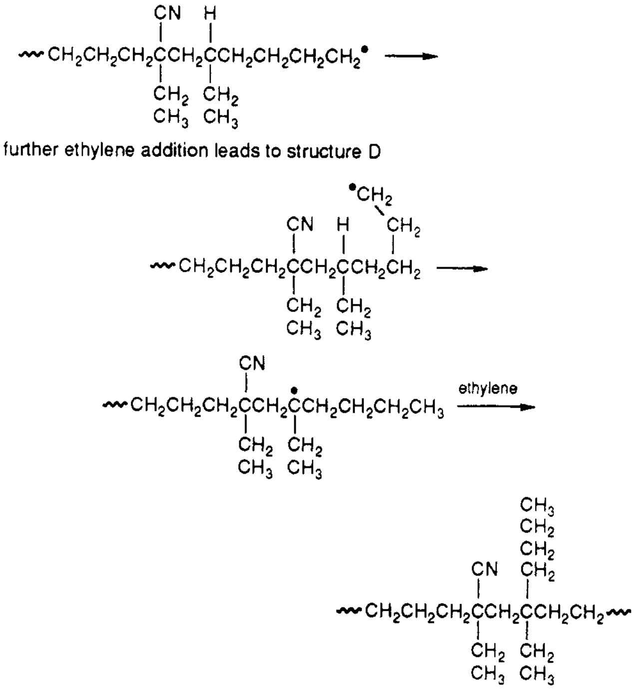


Figure 6. DEPT experiment on the 7.0 mol % E/AN copolymer where only the methine resonances point upward.

The primary source of structural information supporting the existence of structure D is the methylene resonance at 44.80 ppm. The DEPT experiment shown in Figure 6 led to a positive identification of this resonance as arising from a methylene carbon. Its field position at 44.80 ppm is unusually low for *αα* methylene carbon resonances. Typically, *αα* methylene carbons give resonances near 42 ppm[12] when bonded to methine carbons, possessing aliphatic substituents in each direction. These types of methylene carbons would give the lowest field chemical shifts in the carbon-13 NMR spectra of LDPE's, but are normally weak and difficult to observe.[13] The resonance at 44.80 ppm likely originates from an *αα* carbon sandwiched in between a methine carbon and a quaternary carbon. Unfortunately, the $2B_2$ resonance for the ethyl group bonded to the quaternary carbon in structure D, which would be an excellent diagnostic and supporting observation, could not be observed. If it experienced a chemical shift change corresponding to the 2.5 ppm downfield shift for the analogous $4B_4$ carbon in a similarly bonded butyl group in structure B, the $2B_2$ resonance from D would be obscured by the strong $\delta^+\delta^+$ resonance.

The corresponding methine resonances from paired 1,3-diethyl branches typically found in LDPE's are anticipated around 37.4 ppm.[14] These methine resonances were difficult to observe because of overlap with resonances from structure B. The corresponding methyl resonances from such ethyl branches were noted near 11 ppm[14] and are considerably complex. Nitrile carbon resonances are observed at 124.30 and 122.41 ppm. The latter, which is the more intense, is assigned to a nitrile carbon bonded to a tertiary carbon, a requisite for structure A. The weaker nitrile resonance at 124.30 ppm is assigned to nitrile groups bonded to quaternary carbons, a requisite for structures B, C, D, and E. A unique methyl resonance at 8.9 ppm accompanies the appearance of the 44.80 and 124.30 ppm resonances. This resonance is assigned to $1B_2$ carbons arising from ethyl groups bonded to quaternary carbons.[8] The above free-radical pathway leads to structure D, which meets the carbon-13 NMR criteria.

Structure E results from the same back-biting pathways that led to structures B and D, but, in this case, a third back-biting step is required. Again, a similar intermediate cyclic transition state containing five carbon atoms is involved.



A third type of *αα* methylene resonance was unequivocally identified at 47.2 ppm through the DEPT technique. Once again, this chemical shift is at an unusually low field. Consequently, it is assigned to a resonance from a methylene carbon with quaternary carbons as both immediate neighbors. Structure E is produced from three successive back-biting steps and meets this spectral criterion. Structurally, E is quite similar to D; thus considerable overlap is expected for the carbon resonances from these two structures. The important point is that the methylene resonance at 47.2 ppm allows a family of structures to be identified. Overall, the NMR information is consistent with structures produced from single B, double D, and triple E back-biting steps after incorporation of an acrylonitrile unit into a growing polyethylene chain.

Finally, the nitrile resonances also provided information that was diagnostic for structures A–E. The resonance at 124.3 ppm is assigned to a nitrile group bonded to a quaternary carbon. This structural moiety is found in structures B–E. The resonance at 122.41 ppm is assigned to a nitrile group bonded to a methine carbon, which is

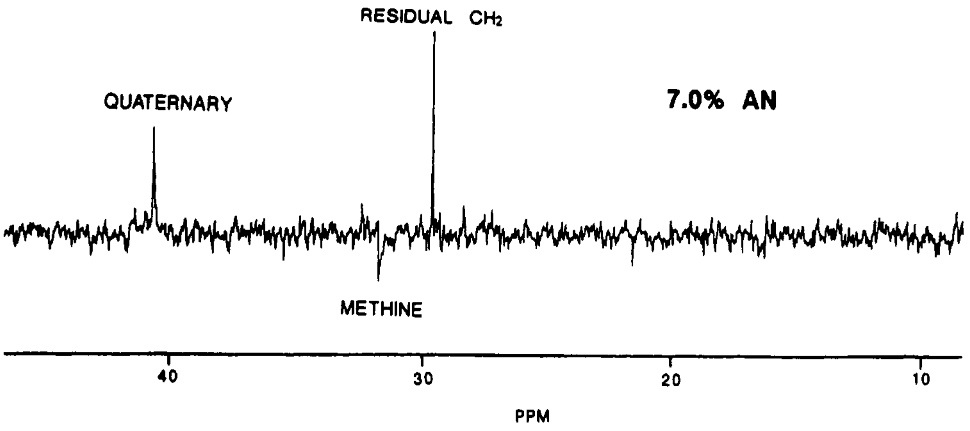


Figure 7. APT experiment on the 7.0 mol % E/AN copolymer. Only the quaternary resonances point upward. All other resonances are nulled.

uniquely found in structure A. A third set of weak resonances at 119.6 and 118.6 ppm could be observed only after utilizing a 20-s pulse delay. The nitrile resonances for atactic polyacrylonitrile occur between 119.5 and 120 ppm,[15] while the 118.6 ppm resonance is anticipated for nitrile carbons bonded to methylene carbons as found in structure C. A longer relaxation time is expected for nitrile carbons at terminal positions of either a branch or long chain, and a 10-s pulse delay proved inadequate for the detection of any terminal nitrile carbon bonded to a methylene group. The presence of nitrile resonances that could be associated with polyacrylonitrile precludes the possibility of the remaining nitrile resonances resulting from configurational isomers of paired acrylonitrile units. In addition, the spacings between these nitrile resonances are greater than that shown in polyacrylonitrile for splittings according to configurational differences,[15] and their growth with acrylonitrile incorporation follows the relative intensity differences observed for structures A–E as evident in Figure 3. Again, no evidence has been obtained for any appreciable quantity of paired acrylonitrile repeat units. All of these nitrile carbon resonances are substantially weaker in intensity than the accompanying carbon resonances from the same structural moieties because they possess intrinsically long relaxation times not satisfied by the chosen acquisition conditions for the NMR experiments. They should, therefore, be used for diagnostic purposes only and not be relied upon for quantitative determinations. Without any other information than that offered by the nitrile resonances, it is clear that these copolymers contain acrylonitrile units incorporated into the copolymer chain in more than one manner.

From an analytical viewpoint, there is an excess of information available for quantitative measurements; consequently some judgement could be exercised by using only the most reliable resonances for quantitative determinations. Region I was not used for quantitative purposes even though it contains three basic types of nitrile resonances that were diagnostic in the structure determinations. Region III was also not used for quantitative purposes because it too arises from quaternary carbons that have relaxation times too long for the chosen NMR acquisition conditions. These copolymer systems produce arrays of resonances for each structural moiety, which lead to a sufficient overdetermination that resonances from carbons with long relaxation times are not required for quantitative measurements. The resonances in the remaining regions, regions II and IV–XIV, arise from methine, methylene, or methyl carbons and the relaxation times of the methylene and methine carbon resonances, in particular, have been satisfied, which permits quantitative use of these relative intensities.

Table IV
Quantitative Distributions of Structures A–E in Ethylene–Acrylonitrile Copolymers Prepared by High-Pressure Free-Radical Polymerization

sample	mol % AN (by ^{13}C NMR)	AN structural dist A	B	C	D	E
1	1.6	64.8	25.4	6.6	3.3	
2	2.5	65.6	26.6	7.9		
3	7.0	67.8	20.0	6.4	3.6	2.2
4	7.5	68.5	21.1	6.6	3.7	
5	10.7	67.7	21.0	6.0	3.4	1.8

The concentration of structure A was measured from the intensities of the 32.82 ($\alpha\delta^+$) and 32.12 ppm (methine) resonances in region VI. There were some problems with overlap from resonances at 32.73 and at 32.21 ppm. An overlap correction was made by determining the relative distribution of these resonances from peak heights and applying this distribution to the total measured area. After overlap correction, the intensity ratio of the peaks at 32.82 and 32.12 ppm was approximately 2:1 as anticipated for structure A.

The concentration of structure B was determined from the intensities of the 37.17 ($\alpha\delta^+$) and 36.79 ppm ($4B_4$) resonances in region IV and the 24.89 ppm ($\beta\delta^+$) resonance in region IX.

The concentration of structure C could only be measured from the well-isolated and characteristic resonance at 17.37 ppm for a methylene group bonded directly to a nitrile group. This resonance would be indicative of either a branch or a chain end terminating with a nitrile group.

The concentrations of the final two structures, D and E, were also determined from single, but well-isolated resonances. Structure D has a key carbon resonance at 44.80 ppm ($\alpha\alpha$ between methine and quaternary carbons), while structure E has a similar key carbon resonance at 47.22 ppm ($\alpha\alpha$ between quaternary carbons). Both are at unusually low fields for methylene resonances and can be conveniently and reliably used for quantitative measurements. Results from the quantitative measurements are given in Table IV for structures A–E, respectively.

One question that comes to mind is, "What effect does the back-biting pathways involving incorporated acrylonitrile units have on the distribution of back-biting structures produced normally in low-density polyethylenes?" In the carbon-13 NMR spectra of these E/AN copolymer samples, there is sufficient spectral information free of overlap to establish the concentrations of the ethyl, butyl, and amyl + longer branches. These branches are in locations that are sufficiently far from a nitrile group to give NMR

Table V
Concentrations of 1,3-Diethyl, Butyl Amyl$^+$, and the Total of Structural Species A–E (S_{AN}) in Branches per 1000 Carbon Atoms in Copolymers of Ethylene and Acrylonitrile Prepared by High-Pressure Free-Radical Polymerization

sample	mol % AN (by NMR)	peak mp, °C	branches per 1000 C atoms 1,3-B_2	B_4	B_5^+	S_{AN}	total disruptions/ 1000 C
1	1.6	107.8	2.0	4.6	2.9	7.9	17.4
2	2.5	107.3	0.5	3.4	2.2	11.4	17.5
3	7.0	90.5	1.9	6.1	1.5	31.5	41.0
4	7.5	95.7	2.2	3.8	0.2	33.9	40.1
5	10.7	66.8	1.0	2.5	3.5	47.6	54.6

chemical shifts corresponding to those observed in low-density polyethylenes. The butyl branch concentration was determined from the $2B_4$ resonance intensity at 23.40 ppm. The amyl + branch concentration was determined from the methine resonance at 38.25 ppm for butyl + longer branches after correcting for the butyl branch contribution. The ethyl branch concentration could only be determined by measuring the entire $1B_2$ area and then subtracting from it the contributions from structures D and E, respectively, that is

$$\text{LDPE-type ethyl branches} = \text{total ethyl branches} - 2(D + E)$$

The LDPE types of alkyl branch concentrations are given in Table V in units of branches per 1000 carbons. The number of new structures involving AN units per 1000 carbons, which was calculated from the concentrations of structures A–E, is also included.

Typically, the short-chain alkyl branch levels in low-density polyethylenes range from 8 to 21 per 1000 carbons.[7-9] The level of corresponding branches in these ethylene–acrylonitrile copolymers varies from approximately 7 to 11 alkyl branches per 1000 carbon atoms. It was of interest to determine the total concentration of "chain disruptions" per 1000 carbons, which would include the nitrile-containing structural moieties plus the normal alkyl branching. This was accomplished through the following relationship:

$$\text{total chain disruptions/1000 carbons} = (1/2)B_2/1000\ \text{C} + B_4/1000\ \text{C} + B_5^+/1000\ \text{C} + S_{AN}/1000\ \text{C}$$

where $S_{AN}/1000$ C represents the chain disruptions created by the new structures created by acrylonitrile additions and is given by

$$S_{AN}/1000\ \text{C} = (A + B + C + D + E)/1000\ \text{C}$$

It was necessary to take one-half of the previously calculated ethyl branch concentrations to determine the contribution of 1,3-diethyl branches as "chain disrupters" because the ethyl branches normally occur in pairs. The ethyl branches are exclusively products of successive back-biting mechanisms. An intermediate cyclic transition state containing only three carbon atoms, which seems an unlikely possibility, is required for the formation of isolated ethyl branches. The absence of isolated ethyl branches is confirmed by the carbon-13 NMR observation of missing resonances at the known chemical shifts for isolated ethyl branches as seen in the carbon-13 NMR spectra of ethylene–1-butene copolymers.[14] The resonances for successive 1,3-diethyl branches are easily identified.[8]

A comparison of $S_{AN}/1000$ C to the "total chain disruptions/1000 C" indicates that the total alkyl branch concentration decreases between 25 and 50% as S_{AN} increases. Sample 1 contains 1.6 mol % acrylonitrile and has 9.5 alkyl branches per 1000 carbons, which is at least 25% below the level seen typically in low-density polyethylenes. This decrease in alkyl branching becomes approximately 50% when the acrylonitrile content approaches 11 mol %. The relative concentrations of ethyl versus butyl branches remain fairly consistent as seen by the data in Table V.

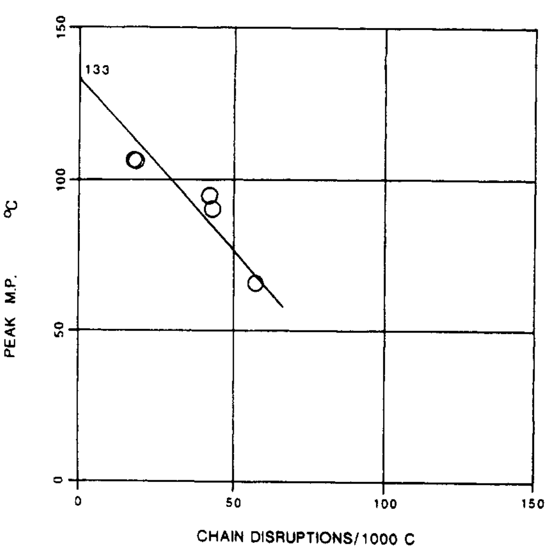
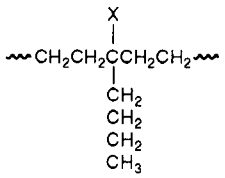


Figure 8. Relationship between peak melting points as estimated from DSC and NMR results for number of chain disruptions per 1000 carbon atoms.

It was of further interest to see if there was any consistency between the "total chain disruptions/per 1000 C" and the "peak" melting points also given in Table V as taken from the DSC data in Figure 1. There is no easy way to determine representative or averaging melting points from copolymer systems like these, which exhibit a broad range of melting behaviors. A rough trend between the highest peaks of the DSC curves and the total chain disruptions/1000 C would suggest that the structural changes among these samples are occurring systematically as the acrylonitrile content increases. This, in fact, was observed as shown by the graph in Figure 8. The line drawn in Figure 8 extrapolates close to 133 °C, which is a characteristic melting point of high-density polyethylene homopolymers. This is an encouraging result for understanding the differences observed among the DSC behaviors of these samples. The NMR data for total chain disruptions does correlate well with the melting behavior as observed by DSC. A correlation between mol percent acrylonitrile and melting behavior should not be expected because the melting points are determined by a number of additional factors, namely, the levels of normal alkyl and long-chain branches in addition to the CN-containing moieties. Thus a correlation between mole percent acrylonitrile and DSC melting behavior would only occur if the number and type of alkyl branches were the same for all of the samples. It is also encouraging that the directional difference in melting points between samples 3 and 4 is predicted by the number of total chain disruptions/1000 C.

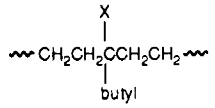
Other Ethylene Copolymers Prepared by High-Pressure Free-Radical Polymerizations

The successive back-biting steps, which led to the various structural moieties, B–E, during free-radical polymerizations of ethylene and acrylonitrile are likely to occur during other high-pressure free-radical copolymerizations involving ethylene and other substituted vinyl monomers. The carbon-13 NMR spectra of copolymers of ethylene and (a) acrylic acid, (b) methyl acrylate, and (c) vinyl acetate were also examined for spectral evidence of structures analogous to B, that is



$\sim\!\sim CH_2CH_2\overset{X}{\underset{CH_2CH_2CH_2CH_3}{C}}CH_2CH_2\sim\!\sim$

The above structure was observed in each of the aforementioned copolymers and at the following levels:

comonomer	X group	wt %  $\sim\!\sim CH_2CH_2\overset{X}{\underset{\text{butyl}}{C}}CH_2CH_2\sim\!\sim$
acrylonitrile	CN	23
acrylic acid	COOH	16
methyl acrylate	$COOCH_3$	10
vinyl acetate	CH_3COO	<3

There is likely a relationship between the nature of the X group and the tendency for the copolymer to undergo these additional back-biting steps. The π bonds of the nitrile and carboxylic acid groups can participate in mesomeric stabilization of the radical generated at the tertiary carbon. Such a stabilization mechanism is not available to the acetate group because this form of delocalization over the σ-bonded heteroatom is precluded. More data will be required from other types of ethylene copolymers and at various comonomer levels before such a trend can be firmly established. It would also be interesting to examine copolymers where this particular back-biting mechanism is blocked by an alkyl substituent, such as in ethylene–methyl methacrylate or ethylene–methacrylic acid copolymers. For the time being, it is important to establish that the various new types of structural moieties produced from successive back-biting steps involving a comonomer unit are not restricted to the ethylene–acrylonitrile copolymer systems.

Conclusions

The existence of a series of Roedel back-biting steps, which lead to complex 1,1, 1,3, 1,3,3, and 1,3,3,5, etc., branched structures, can involve incorporated comonomer units during high-pressure free-radical polymerizations of ethylene. These structures contain ethyl and butyl branches because the subsequent additional back-biting steps must produce alkyl branches involving some multiple of 2. Amyl branches are thus precluded after the occurrence of an initial back-biting step. There are some significant points concerning the copolymerization of ethylene and acrylonitrile through high-pressure free-radical processes established by this study. First, the incorporation of acrylonitrile occurred systematically with increasing acrylonitrile concentrations even though the overall product yields were exceedingly low. The effect on melting point behavior was dramatic, but it resulted only from an increase in the same type of chemistry that occurred at the lowest acrylonitrile levels. The five structural moieties identified in these copolymers remained at almost the same distribution irrespective of the total acrylonitrile content. Secondly, acrylonitrile was incorporated randomly through an ethylene–acrylonitrile–ethylene series of additions. Three of the four new acrylonitrile-containing structural moieties resulted from back-biting after a normal addition of acrylonitrile. Only one was produced by chain transfer involving a terminal acrylonitrile radical before an addition of ethylene. It is interesting to observe that the series of new structures involving comonomer units could be explained by the formation of five carbon atom (six-membered) intermediate cyclic transition states during intramolecular chain-transfer reactions. Such intermediates lead to either butyl or ethyl branches exclusively after an initial back-biting step has occurred. The percent of the back-biting steps involving a transfer of the radical site back to a carbon bearing a nitrile group ranged from 45% at an AN concentration of 1.6 mol % to 87% at an AN concentration of 10.7 mol %. The radical bearing a CN group is expected to be more stable, and consequently less reactive, because of mesomeric interactions, which would enhance the probability of the back-biting chemistry. Some improvement in yields and molecular weight should be anticipated by blocking this particular free-radical pathway through the incorporation of a methyl group or other substituent on the same carbon atom bearing the nitrile group. Methacrylonitrile could be used for this purpose. Vinyl acetate, which is a frequently used comonomer in high-pressure free-radical ethylene polymerizations, shows essentially no tendency to undergo a corresponding type of back-biting chemistry. Hopefully, further studies of copolymers of ethylene and polar comonomers, produced in high-pressure processes, will lead to more definitive conclusions concerning how and when the free-radical back-biting chemistry involving comonomer units occurs.

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(13) Reference 3, p 302.
(14) Reference 3, p 258.
(15) Reference 4, p 131.

Registry No. (Ethylene)(acrylonitrile) (copolymer), 25134-58-1; (ethylene)(acrylic acid) (copolymer), 9010-77-9; (ethylene)(methyl acrylate) (copolymer), 25103-74-6; (ethylene)(vinyl acetate) (copolymer), 24937-78-8.