

# The Identity of the Amyl Branch in Low-Density Polyethylenes

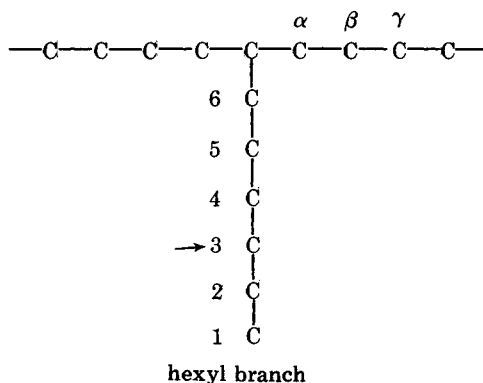
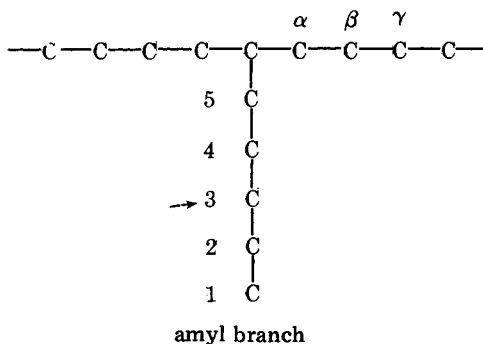
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## Synopsis

Amyl branches have been positively identified as one of the principal short short chain branches in low density polyethylenes prepared by high pressure processes.

In a recent  $^{13}\text{C}$  NMR study of low-density polyethylenes, Cudby and Bunn<sup>1</sup> claimed that they could not recognize separately amyl branches from ethyl, butyl, and longer chain branches. As pointed out in their work and previously in the work of others, the butyl branch generally dominates the branch distribution,<sup>1-4</sup> as the exact short-chain branch distribution is affected by reaction conditions.<sup>1</sup> They were not convinced, however, by the evidence obtained from a study of ethylene-1-olefin copolymers<sup>2</sup> that the amyl branch could be identified using  $^{13}\text{C}$  NMR data from ethyl, butyl, and other long-chain branches possible in low-density polyethylenes.

The identity of the amyl branch was originally based on the existence of separate carbon-3 resonances from amyl and hexyl<sup>+</sup> longer branches, that is,



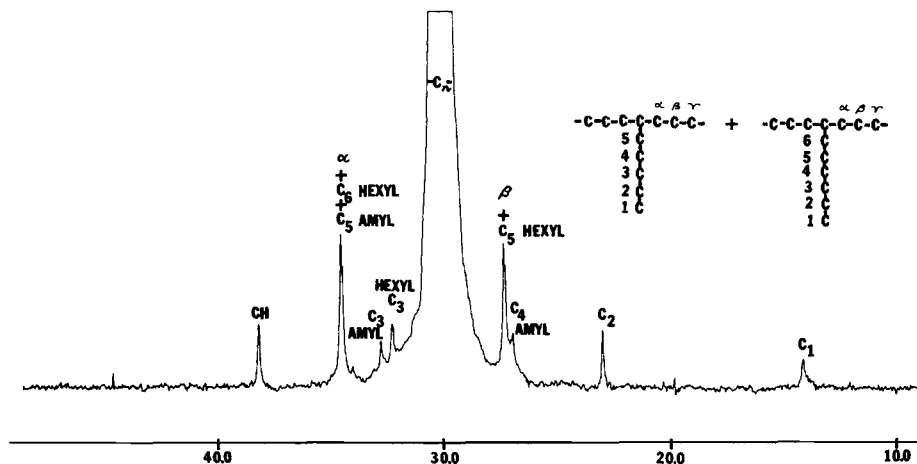


Fig. 1. Carbon-13 NMR Spectrum of a mixture of ethylene-1-heptene and ethylene-1-octene copolymers. Chemical shifts are in ppm from TMS.

It can be shown with the Grant and Paul parameters<sup>5</sup> that the carbon-3 chemical shifts will be the same for all branches six carbons in length and longer. A separate resonance is expected for the amyl branch that is unique and differs from that from six-carbon branches by the magnitude of the  $\delta$  carbon contribution:

$$(\delta_3)_{\text{amyl}} = 2\alpha + 2\beta + \gamma + 2\delta + 2\epsilon + \text{constant} = 32.89 \text{ ppm}$$

$$(\delta_3)_{\text{hexyl}} = 2\alpha + 2\beta + \gamma + \delta + 2\epsilon + \text{constant} = 32.52 \text{ ppm}$$

The Grant and Paul calculated chemical shifts above were obtained with recent polymer values determined from a series of ethylene-1-olefin copolymers and hydrogenated polybutadienes.<sup>6</sup> The original  $\delta$  parameter reported by Grant and Paul had a value of 0.31 ppm, while Carman et al.<sup>7</sup> obtained a value of 0.28 ppm in a related study that extended the number of alkanes used in the least-squares analysis. Thus, a chemical shift difference is predicted that should be observable on most modern high-resolution NMR spectrometers. In fact, two resonances, with appropriate chemical shifts and separation for the carbon-3's in amyl versus hexyl branches, have been observed in the <sup>13</sup>C NMR spectra of low-density polyethylenes.<sup>2,4</sup>

The ethylene-1-heptene and ethylene-1-octene copolymers are excellent model polymers for a determination of the carbon-3 chemical shifts for the amyl and hexyl branches, respectively. In the original analysis,<sup>2</sup> the <sup>13</sup>C NMR spectra were obtained separately and the chemical shifts compared. For the purpose of confirming the existence of separate carbon-3 resonances for amyl and hexyl branches, it may be better to prepare a blend of the two copolymer samples and obtain a <sup>13</sup>C spectrum under precisely the same experimental conditions. A blend was prepared by dissolving 2:1 weights of ethylene-1-heptene and ethylene-1-octene copolymers into a mixture of 1,2,4-trichlorobenzene and perdeuterobenzene. (These copolymers did not have equal 1-olefin contents as the 1-octene copolymer has a higher branching content than does the 1-heptene copolymer.) The final concentration was approximately 15% (total polymer) by

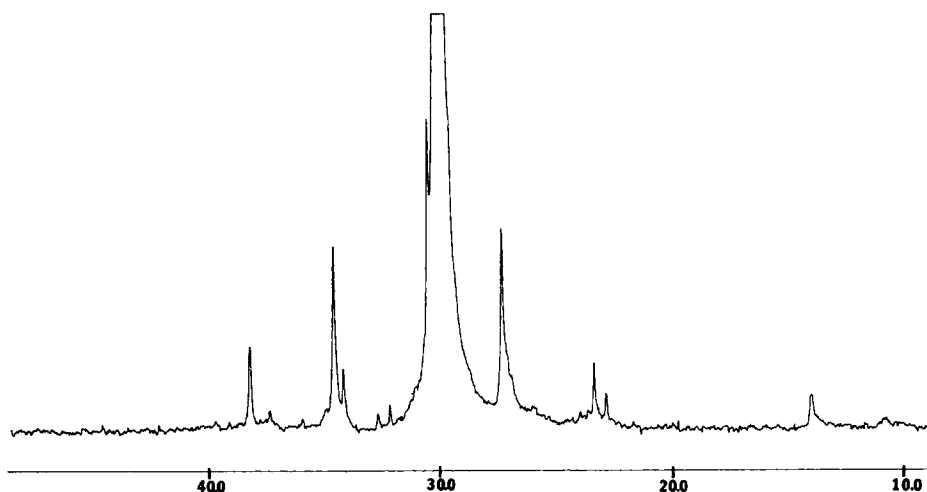


Fig. 2. Carbon-13 NMR Spectrum of a low-density polyethylene containing amyl branches in addition to ethyl, butyl, and longer-chain branches. Chemical shifts are in ppm from TMS.

weight. Sufficient perdeuterobenzene was present to maintain an internal lock signal at 125°C. Separate carbon-3 signals are obtained, as is clearly shown in the <sup>13</sup>C NMR spectrum of the blend in Figure 1. A spectrum of a low-density polyethylene showing corresponding carbon-3 resonances is given in Figure 2. Thus, low-density polyethylenes prepared in high-pressure processes can contain amyl branches in addition to butyl and ethyl. In addition, Bovey has shown that the carbon-3 resonance from hexyl<sup>+</sup> branches in low-density polyethylenes can, at least for some low-density polyethylenes, be attributed almost entirely to long-chain branching.<sup>4</sup>

Another question raised by Cudby and Bunn is whether separate methyl resonances should also be observed for amyl and hexyl branches. Differences were reported for these methyl chemical shifts as observed independently in the <sup>13</sup>C spectra of the ethylene-1-heptene and ethylene-1-octene copolymers.<sup>2</sup> These differences are not anticipated through calculated chemical shifts, as shown in

TABLE I

| Carbon            | Calculated ethylene-1-heptene copolymer | Calculated ethylene-1-octene copolymer | Observed copolymers | Low-density polyethylenes |
|-------------------|---|--|---------------------|---------------------------|
| Methine           | 38.00                                   | 38.00                                  | 38.17               | 38.22                     |
| α                 | 34.89                                   | 34.89                                  | 34.52               | 34.59                     |
| β                 | 27.56                                   | 27.56                                  | 27.32               | 27.34                     |
| C-5 (amyl)        | 34.83                                   |  |                     |                           |
| C-6 (hexyl)       |   | 34.89                                  | 34.52               | 34.59                     |
| C-4 (amyl)        | 27.13                                   |  | 26.93               | 26.96 (s)                 |
| C-5 (hexyl)       |   | 27.50                                  | 27.32               | 27.34                     |
| C-4 (hexyl)       |   | 30.01                                  | 30.08               | 30.03                     |
| C-3 (amyl)        | 32.89                                   |  | 32.75               | 32.72                     |
| C-3 (hexyl)       |   | 32.52                                  | 32.26               | 32.21                     |
| C-3 (amyl, hexyl) | 22.74                                   | 22.68                                  | 22.98               | 22.91                     |
| C-1 (amyl, hexyl) | 14.07                                   | 14.07                                  | 14.19               | 14.12                     |

Table I, with the Grant and Paul parameters but are probably related to the difficulties in measuring chemical shifts in spectra that contain a biased baseline since the spectrum of the blend showed no differences in the methyl chemical shifts. The spectra presented here were obtained with a 16K computer system which eliminated many of the problems encountered in the early spectra.

The only other source of identification of amyl versus longer-chain branches is possibly in the carbon-4 resonance which occurs near 27 ppm. A separate amyl carbon resonance is predicted by the calculated chemical shifts, in Table I, that is observed in the spectrum of the copolymer blend. Unfortunately, this resonance is not distinctly separated from the stronger 27.5 ppm resonance in Figure 1 and appears only as a shoulder in Figure 2. Part of the difficulty with low-density polyethylenes may occur from the  $\beta$ -carbon resonance from ethyl branches which is predicted at 27.38 ppm and should lie between the carbon-4 resonance from amyl branches and the stronger  $\beta$ -carbon resonance from butyl and longer branches. Thus, the 27–28 ppm range in the  $^{13}\text{C}$  NMR spectra of low-density polyethylenes, under appropriate circumstances, could lead to information about the branch length distribution, but generally will not lead to such clear-cut results as do the resonances from the carbon-3's.

Nevertheless, the identification of amyl branches can be made with certainty from the carbon-3 chemical shifts in  $^{13}\text{C}$  NMR spectra. The resonance near 32.6–32.8 ppm can be easily distinguished apart from the corresponding resonance from hexyl<sup>+</sup> longer-chain branches. Although the exact chemical shifts were not reported, amyl branches may be present in three of the four low-density polyethylenes presented in the study by Cudby and Bunn. The identity of amyl branches is important since it shows that both five- and six-membered transition states are occurring during the intramolecular chain transfer process that produces short-chain branches in low-density polyethylenes.

### References

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Received August 10, 1976

Revised December 17, 1976