

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Short-Chain Branching in Polyethylene and Poly(vinyl Chloride) Using Pyrolysis Hydrogenation Gas Chromatography and ^{13}C Nuclear Magnetic Resonance Analysis

S. A. Liebman^{ab}; D. H. Ahlstrom^a; W. H. Starnes JR.^c; F. C. Schilling^c

^a Research and Development Center, Armstrong World Industries, Inc., Lancaster, Pennsylvania ^b Chemical Data Systems, Inc., Oxford, Pennsylvania ^c Bell Laboratories, Murray Hill, New Jersey

To cite this Article Liebman, S. A. , Ahlstrom, D. H. , Starnes JR., W. H. and Schilling, F. C.(1982) 'Short-Chain Branching in Polyethylene and Poly(vinyl Chloride) Using Pyrolysis Hydrogenation Gas Chromatography and ^{13}C Nuclear Magnetic Resonance Analysis', *Journal of Macromolecular Science, Part A*, 17: 6, 935 – 950

To link to this Article: DOI: 10.1080/00222338208056494

URL: <http://dx.doi.org/10.1080/00222338208056494>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Short-Chain Branching in Polyethylene and Poly(vinyl Chloride) Using Pyrolysis Hydrogenation Gas Chromatography and ^{13}C Nuclear Magnetic Resonance Analysis

S. A. LIEBMAN* and D. H. AHLSTROM

Research and Development Center
Armstrong World Industries, Inc.
Lancaster, Pennsylvania 17604

W. H. STARNES, JR., and F. C. SCHILLING

Bell Laboratories
Murray Hill, New Jersey 07974

ABSTRACT

This study compares the use of pyrolysis hydrogenation gas chromatography (PHGC) and ^{13}C Fourier transform nuclear magnetic resonance (FTNMR) methods for the analysis of reference polyethylene (PE) samples, ethylene- α -olefin copolymers, and specially prepared poly(vinyl chloride) (PVC) samples which were reduced to their PE skeletal structures. The nature and relative quantities of the short branches along the polymer chains were determined using both techniques. Improved high-resolution PHGC data, obtained with a fused silica capillary separation column, gave results which were in satisfactory agreement with the ^{13}C FTNMR data. This approach confirms that detailed

*Present address: Chemical Data Systems, Inc., Oxford, Pennsylvania 19363.

microstructural information can be obtained with these methods by using carefully controlled experimental conditions and appropriate reference systems.

INTRODUCTION

Our earlier PGC (pyrolysis gas chromatography) and PHGC work using packed GC columns [1] was concerned with the study of short-chain branches in the title compounds and gave results that were somewhat at variance with published ^{13}C NMR data. Also, in connection with this study, literature results obtained by others using analytical pyrolysis, infrared (IR), ^{13}C FTNMR, and radiolysis methods, were reviewed [1]. At the time, correlations between techniques were variable, in part owing to the use of polymers from different sources and in part to the state-of-the-art limitations in spectroscopy and analytical pyrolysis. Each methodology was restricted by its associated instrumental and interpretive capabilities. The present work addresses the problems of differing samples and methodologies by using the same source samples for examination with improved capillary-column PHGC instrumentation and careful attention to ^{13}C FTNMR experimental conditions. In this manner we intend to determine the qualitative and quantitative branch contents of different PE's and reduced PVC's and to correlate the results obtained from the two analytical approaches.

Since 1976, many researchers have contributed to the understanding of polymer microstructure in similar systems. In addition to improved analytical pyrolysis and ^{13}C FTNMR experimentation, better IR methods have been employed. Many systems may now be examined by these analytical tools to obtain both qualitative and quantitative microstructural information. Since sample requirements vary considerably for each form of instrumentation, it is desirable to have reliable and relatable analyses from the various techniques. Depending upon the specific problem-solving situations and laboratory environments involved, any one or all of the tools may then be used to provide the necessary information. The following discussion summarizes some of the important developments that have occurred since our previous publication [1].

In 1976 Cudby and Bunn [2] used IR and ^{13}C FTNMR to study four low-density PE (LDPE) samples. The IR analyses allowed the determination of total branches (having a CH_3 end) for the various samples and gave values that ranged from 23 to 37 methyl/1000 CH_2 . The ^{13}C FTNMR method further differentiated the branch content to show ranges of 10 to 14 n-butyl/1000 CH_2 , < 1 to 11 ethyl/1000 CH_2 , and 8 to 21 "longer" branches/1000 CH_2 in this PE series. In another IR study using an improved method for spectral compensation and appropriate spectral assignments, McRae and Maddams [3] determined the total number of branches ending in methyl (corrected for chain-end

methyls) in a series of nearly linear PE's. These high-density PE (HDPE) samples showed only methyl branches in a range of ~1 to 5 methyl/1000 CH₂; no ethyl or n-butyl branches were detected. Also in 1976, Cheng, Schilling, and Bovey [4] reported ¹³C FTNMR results for two LDPE samples. No methyl branches were detected in either material, but average values of 11 n-butyl, 2 ethyl, 3 n-amyl, and 4 "long" branches/1000 CH₂ were found. Values of ~5-6 n-butyl, 1 ethyl, 2 n-amyl, and 1 "long" branch/1000 CH₂ were determined in another ¹³C FTNMR study by Bovey et al. [5] that was performed on two LDPE fractions. In this work [5], the "long"-branch concentrations were also deduced from viscosity measurements, which gave values that were in good agreement with those obtained by the NMR technique.

In 1977 Cutler et al. [6] reported ¹³C NMR results and the use of an IR computer deconvolution method in a study of high-pressure polymerized PE. Data were obtained for three different LDPE's whose branch contents ranged from 14 to 22 n-butyl, 11 to 21 ethyl, and 12 to 17 "longer" branches/1000 CH₂. Also during 1977, Bowmer and O'Donnell [7] used radiolysis, IR, and ¹³C NMR techniques to study several PE samples. The IR data (corrected for chain-end methyls) gave 27 and 31 methyl/1000 CH₂ for the respective LDPE's and 1.6 methyl/1000 CH₂ for a sample of HDPE. Their ¹³C NMR analyses [7] delineated the specific branch type of the two LDPE's as 67.3, 65.7% n-butyl; 11.8, 11.2% n-amyl; 7.6, 10.0% ethyl; 5.4, 5.5% n-hexyl + longer; 3.8, 3.7% 2-ethyl-n-hexyl; and 3.8, 3.7% 1,3-diethyl branches, respectively.

Importantly, in 1977 Axelson, Mandelkern, and Levy [8] studied the ¹³C spin relaxation parameters of branched PE's and discussed the necessary conditions for proper quantitative experimentation. The spin-lattice relaxation times of some of the carbons associated with branches were found to be relatively long; thus long delays between scans are needed if the resonances of these carbons are to be used for quantitative branch determinations. Full nuclear Overhauser enhancement factors were obtained for all of the resonances measured. In 1979, from a study of many LDPE samples, these workers [9] were also able to reaffirm the commonly held belief that there is no typical LDPE system insofar as the type, concentration, and distribution of branches are concerned. Nevertheless, there seems to be general agreement in the recent literature that n-butyl branches usually predominate in LDPE.

In 1979, Bovey et al. [10], using optimized ¹³C FTNMR conditions, reported the analysis of a LDPE containing 10.9 n-butyl, 2.5 ethyl, 3.7 n-amyl, and 4.5 n-hexyl and/or longer branches/1000 CH₂. Using PHGC, Sugimura and Tsuge [11] presented data in 1979 for two LDPE samples. Improved instrumentation with capillary columns was employed for this work. The total methyl-branch contents determined by an IR method were 28.5 and 29.3/1000 CH₂, and the PHGC method further delineated the types and relative amounts of branches, which were n-butyl > ethyl > methyl, and n-butyl > ethyl = methyl, respectively, for the two samples studied.

TABLE 1. Branch Contents Reported in the Recent Literature for Various LDPE and HDPE Samples

| Sample | Method | Branches/1000 CH ₂ | | | | | | | Refs. |
|---------------------------|-------------------------|-------------------------------|---|--------------------------------------|----------------------|---------|----------|----|-------|
| | | Total methyl | Methyl | Ethyl | n-Butyl | n-Amyl | "Long" | | |
| 4 LDPE's | IR, ¹³ C NMR | 23-37 | - | < 1-11 | 10-14 | - | 8-21 | 2 | |
| 5 HDPE's | IR | 1-5 | - | - | - | - | - | 3 | |
| 2 LDPE's | ¹³ C NMR | - | - | 1,9,2,6 | 9,7,11,4 | 2,1,4,4 | 3,4,4,1 | 4 | |
| 3 LDPE's | ¹³ C NMR | - | - | 11,14,21 | 14,17,22 | - | 12,14,17 | 6 | |
| 2 LDPE's | IR, ¹³ C NMR | 27,31 | - | 2,3 | 18,20 | 3,3,5 | 1,5,2 | 7 | |
| 1 HDPE | IR | 1.6 | 1.6 | - | - | - | - | - | |
| 1 LDPE | ¹³ C NMR | - | - | 2,5 | 10,9 | 3,7 | 4,5 | 10 | |
| 2 LDPE's | IR, PHGC | 28.5,29.3 | - n-butyl > ethyl n-butyl > ethyl = methyl | > ethyl > methyl > ethyl = methyl | > methyl = methyl | - | - | 11 | |
| 21 LPDE's D and HDPE's | IR | 0.5-67 | - | - | - | - | - | 24 | |
| 4 HDPE's | ¹³ C NMR | - | 0.4-2.6 | - | - | - | - | a | |

^a J. Spěváček, Polymer, **19**, 1149 (1978).

Table 1 summarizes the data discussed above and also contains other analytical results that have appeared in the recent literature. We wish to emphasize that this summary is intended to be representative rather than all-inclusive.

Analogous information on the branch content of PVC [12, 13] and reduced PVC [10, 14-17] has also been published recently. The tri-n-butyltin hydride or deuteride reduction method [14] has proven to be especially advantageous for the study of PVC systems. In general, reduced-PVC samples have shown a low order of methyl branching (~ 2 to 3 methyl/1000 CH_2) and even fewer ethyl or n-butyl branches [1, 15, 18]. Earlier work [19-21] and recent studies [15, 18] have shown that the degree of monomer conversion and the temperature of polymerization influence the nature and number of the branches to only a small extent. In 1979 Starnes et al., using ^{13}C FTNMR, reported the presence of tertiary chloride at all of the long-branch points of a polymer that had been prepared by polymerization in bulk at 100°C [10, 16]. This sample (reduced) and a reduced PVC (S-54 [22]) similar to that used in an earlier PGC/PHGC investigation [1] were included in the present PHGC and ^{13}C FTNMR comparative study.

In summary, it has been shown that significant advances have been made within the past few years in the spectroscopic and chromatographic analyses of branch content in the systems discussed herein. The current Fourier transform IR (FTIR) instrumentation makes quantitative analysis even more readily achievable [23] and removes some limitations on the IR band compensation and deconvolution [24] approaches. Although ^{13}C FTNMR analysis has great value in microstructural studies, the possibility of applying this technique in order to determine the branch contents of solid PE samples, using cross-polarization and magic-angle spinning, does not appear promising at this time [25]. Inherent limitations and complexities in relaxation phenomena may preclude the trace detection of specific branch structures using this approach. On the other hand, excellent results were shown recently [26] in a ^{13}C NMR spectrum obtained on a wide-bore NT-200 (4.7 T) spectrometer using a 20-mm sample tube containing a minimal amount of o-dichlorobenzene that had been added to swell a commercial LDPE sample. With a total data accumulation time of only 12.6 min, the analysis determined branch structures and end-groups in the concentration range of 7/10,000 CH_2 . Interestingly, the ethyl branch content (0.32%) was greater than the n-butyl branch content (0.07%) of the sample studied. In addition, the PHGC and PGC methods have also shown notable improvements in instrumentation. Although these methods require minimal sample size and preparation, it appears that their detection limits for short branches are also being approached at a few per 10,000 CH_2 units.

EXPERIMENTAL

HDPE and LDPE samples (SRM 1475 and SRM 1476, respectively) were obtained from the National Bureau of Standards (NBS); linear

PE (Marlex 50) was obtained from the Phillips Petroleum Company. Ethylene-butene and ethylene-hexene copolymers were received from various commercial sources. Vinyl chloride was bulk polymerized at 100°C, and the polymer was reduced with tri-*n*-butyltin hydride in the manner described elsewhere [14, 15, 18]. A sample of S-54 PVC [22], obtained from K. B. Abbäs, was also reduced in this way.

PHGC experiments were conducted using a Hewlett-Packard 5710A GC instrument equipped with a flame ionization detector and a flexible fused-silica capillary column, 0.22 mm × 50 m, wall-coated with OV-101 (Scientific Glass Engineering, Inc., Austin, Texas 78759). The GC unit was modified for capillary columns using an all-glass-lined splitter system, manufactured by J&W Scientific Corporation, Rancho Cordova, California 95670, and purchased from Supelco, Inc., Bellefonte, Pennsylvania 16823. Pyrolysis was carried out using a Pyroprobe Model 190 unit (Chemical Data Systems, Inc., Oxford, Pennsylvania 19363) with ~0.5 mg of sample and pulsing for 10 s at either 700 or 725°C (as indicated below) with the interface temperature set at 220°C. The pyrolysate was swept by the hydrogen carrier gas into a 4 mm × 5 cm catalyst bed of Pd on Chromosorb P contained in the modified glass injection port, which was maintained at 250°C. The PHGC data are estimated to be reproducible to better than ±2% for all significant peaks.

Carbon-13 FTNMR data for the reference PE's and copolymers and for the reduced PVC's were obtained at 25 MHz on a Varian XL-100 spectrometer modified for pulse Fourier transform operation and interfaced with a Nicolet Model 1080 computer. Samples were examined at 110°C in 1,2,4-trichlorobenzene solution using a 90° pulse angle and pulse intervals that were of sufficient length to permit the quantitative measurement of the branch contents of the polymers. Broad band noise decoupling was employed in order to decouple protons from the carbon nuclei, and hexamethyldisiloxane was used as an internal reference. Further details and spectral data for the reduced PVC's are given in Refs. 10, 14, 15, and 18.

The GC computer simulation program was written by Roeser [27] for the DEC System 10 (Digital Equipment Corporation, Maynard, Massachusetts 01752), which was equipped with a GT-40 graphics terminal and a Benson-Lerner CID 305 plotter. The pyrograms were digitized with a unit manufactured by Altex Corporation, Silver Springs, Maryland 20904. Data manipulation was performed with a FORTRAN-10 computer program written for a maximum of three pyrograms. Either full or partial patterns could be manipulated by adding specific peaks in Patterns 1 and 2 to those corresponding in Pattern 3 at various weighted levels. Trial-and-error combinations were checked on either the graphic display or with hard-copy plots.

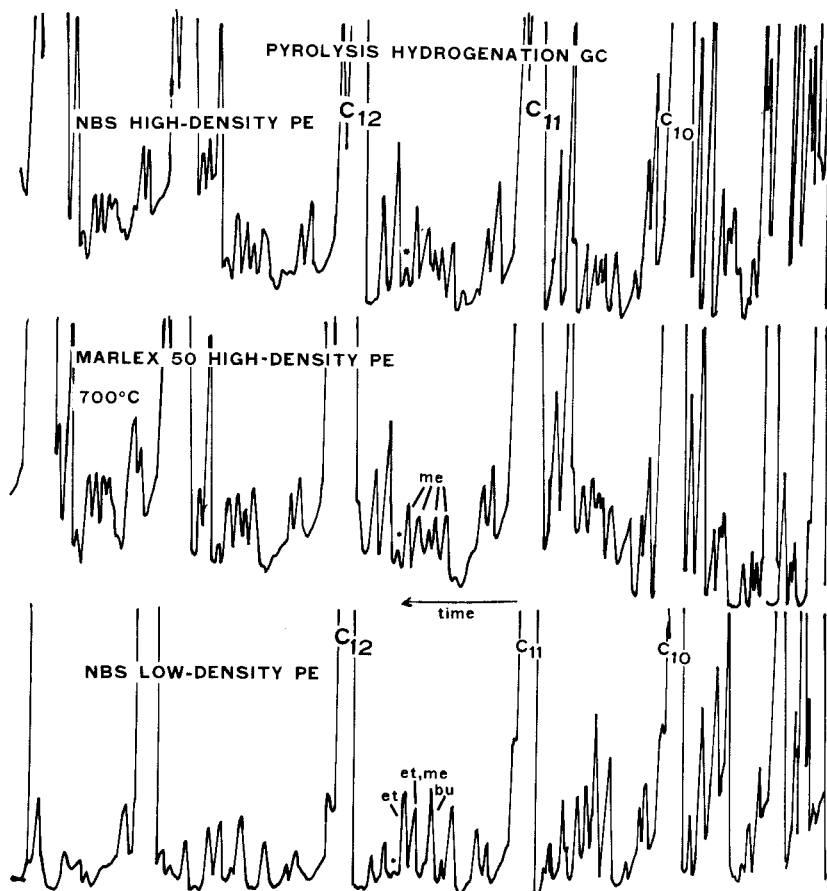


FIG. 1. Pyrograms of two reference HDPE's and a LDPE. All samples were pulsed at 700°C for 10 s.

RESULTS AND DISCUSSION

Pyrograms of the reference PE samples chosen for the present qualitative and quantitative analyses of branch content are shown in Fig. 1. Small but reproducible differences can be detected between the two HDPE's from different sources. These variations in the pyrograms may be ascribed to minor differences in the very low methyl, ethyl, or n-butyl contents. It appears that Marlex 50 is the more nearly linear system, containing only methyl branches (~ 1 methyl/1000 CH_2), while the NBS HDPE has ~ 1 methyl/1000 CH_2 and

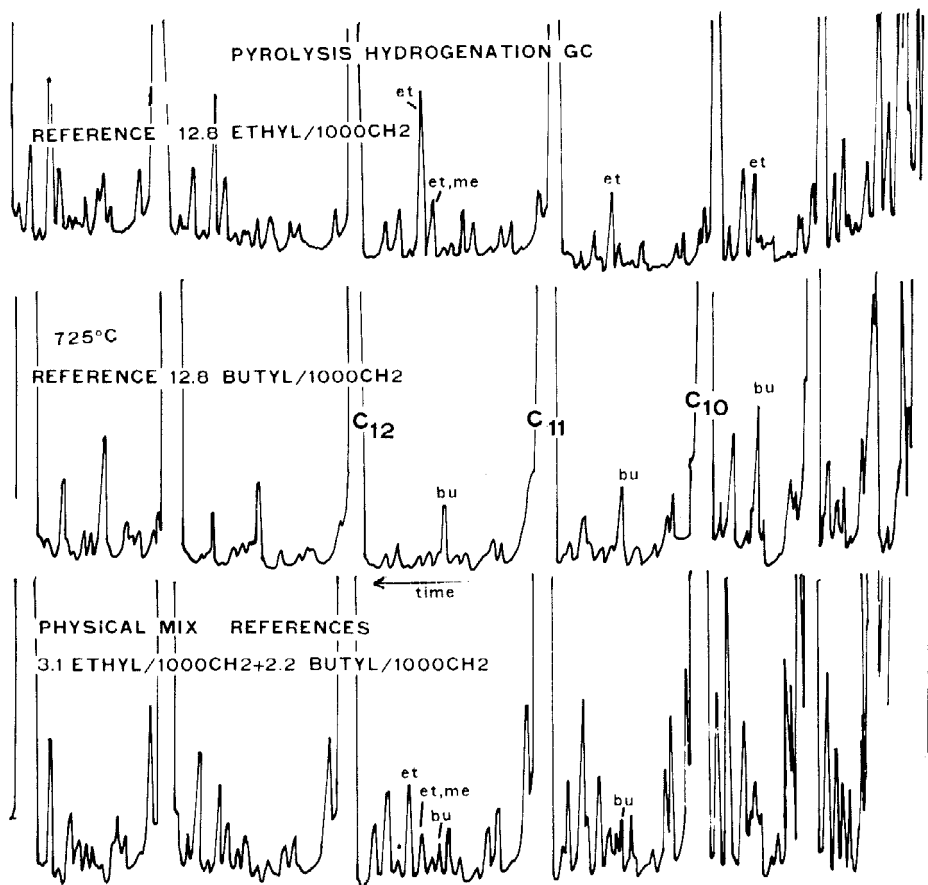


FIG. 2. Pyrograms of reference copolymers and a reference copolymer mixture. Top, ethylene-butene copolymer; center, ethylene-hexene copolymer; bottom, physical mixture of ethylene-butene and ethylene-hexene copolymers. Branch contents of the copolymers (determined by ^{13}C FTNMR) are as indicated; all samples were pulsed at 725°C for 10 s.

probably some low amount of ethyl or n-butyl branches. This interpretation is reinforced by the results, discussed below, that were obtained from the new computer simulation program.

The branched LDPE NBS sample is known to contain significant amounts of n-butyl and ethyl branches (two fractions have been shown to contain about 10 total branches/1000 CH_2 [5]). Figure 2 presents

the pyrograms for some copolymer references examined under identical PHGC conditions: an ethylene-butene copolymer with known ethyl-branch content (12.8 ethyl/1000 CH₂), an ethylene-hexene copolymer with known n-butyl-branch content (12.8 n-butyl/1000 CH₂), and a 1:1 physical mixture of two reference copolymers containing 3.1 ethyl/1000 CH₂ and 2.2 n-butyl/1000 CH₂, respectively. Under our pyrolysis conditions, the response of the diagnostic peaks for ethyl content (3-methyl- and 3-ethylalkanes) was more than three times as intense as the response of the diagnostic peaks corresponding to n-butyl content (5-methyl- and 5-ethylalkanes). On this basis, n-butyl branches predominate over ethyl branches in NBS LDPE by PHGC data for this sample to give estimated branch contents of 10 n-butyl and 3 ethyl/1000 CH₂.

Figure 3 records the pyrograms of the two reduced-PVC samples that were identified above. Comparative analyses of the PHGC data shown in Figs. 1-3 permitted determination of the short-branch contents in the reduced-PVC systems. The isoalkane fragmentation patterns in Figs. 1 and 2 between the C₉ and C₁₂ n-alkane peaks were useful for this purpose. Somewhat improved diagnostic patterns resulted when the pyrolyses were performed at 700°C rather than 725°C (Fig. 3). The diagnostic fragments for the determination of methyl branches (2-methylalkanes) and those for ethyl content (3-methyl- and 3-ethylalkanes) are slightly enhanced peaks in the reduced-PVC pyrograms relative to those in the series of selected reference pyrograms.

It was thus estimated that both reduced-PVC samples contain ~ 3 methyl branches/1000 CH₂ and a somewhat lower number of ethyl branches (≤ 1 ethyl/1000 CH₂). Likewise, the presence of a low number of n-butyl branches is indicated for both reduced-PVC systems: ~ ≤ 1 n-butyl/1000 CH₂. This value is estimated from the enhanced diagnostic peak of the 5-methylalkanes in the respective pyrograms (Fig. 3). "Long" branches were not studied in this PHGC analysis, nor was the detection of n-amyl branches considered, although these structures can be determined by the ¹³C NMR technique. It should also be noted that a unique PHGC fragmentation peak (denoted by * in the figures) was enhanced only for the reduced PVC samples, but not for any reference materials. Further work is in progress in order to determine the significance of the unassigned fragment peak.

Correspondingly, ¹³C FTNMR data were obtained on the reduced suspension-polymerized PVC (S-54) and on the reduced 100°C bulk-polymerized polymer under conditions designed to allow detection and quantitative measurement of the short-branch contents of these materials. In order to minimize any possible errors resulting from differences in spin-lattice relaxation times [8], all branch contents were calculated from the relative intensities of the signals of the backbone carbons that are alpha to branching points. In this way, the following short-branch contents were found (± 0.1/1000 CH₂): reduced PVC, S-54: 2.8 methyl, 0.7 ethyl/1000 CH₂; reduced 100°C

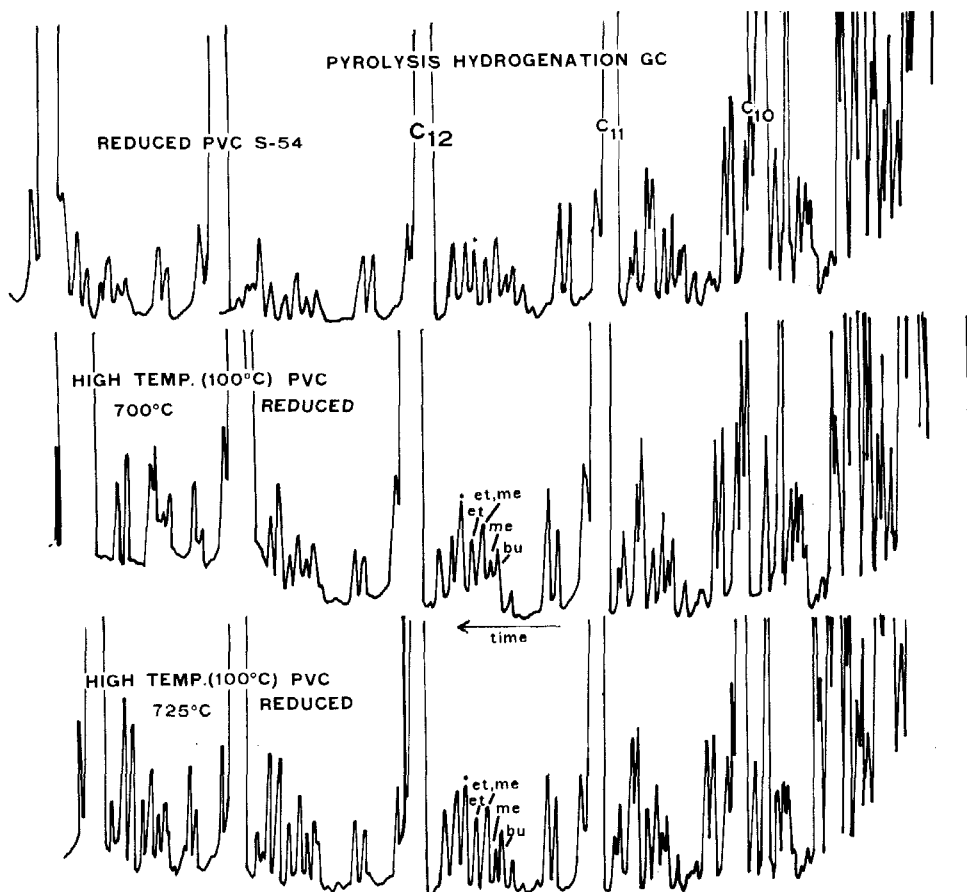


FIG. 3. Pyrograms of reduced PVC's. The top and center samples were pulsed at 700°C for 10 s; the bottom sample was pulsed at 725°C for 10 s.

PVC: 2.0 methyl, 0.8 ethyl/1000 CH₂ [18]. The ¹³C NMR spectra also gave strong indications for the presence of isolated n-butyl branches in these polymers, although the evidence was not conclusive. Further work is required on this aspect of the structures, which may have confirmation from the PHGC computer simulation results discussed below. In any event, if n-butyl branches are present, the FTNMR and PHGC data both show that their concentrations can be no greater than ~1/1000 CH₂ in the two polymers studied. No FTNMR evidence was obtained for the presence of isolated n-propyl or n-amyl branches in the reduced PVC's. Hence the FTNMR data for these polymers are in reasonable agreement with the PHGC results described above.

From the PHGC and FTNMR observations, we have determined the types and relative amounts of the short branches in selected PE's and reduced-PVC samples. To substantiate these determinations and extend our interpretive capabilities, a computer program was written [27] to enable the use of digitized pyrograms as input and allow the combination of certain selected portions of the pyrograms in order to match the fragmentation patterns of knowns with that of the desired unknown. This computer simulation aid made possible the interpretation of very minor (but reproducible) variations in the experimental PHGC patterns. Figure 4 shows the experimental pyrogram from NBS HDPE and a computer simulation of the pyrogram altered between n-C₁₁ and n-C₁₂. This simulation was accomplished by using the Marlex "base" pattern between C₁₁ and C₁₂ and superimposing upon it a small amount of the diagnostic isoalkane peaks from the ethyl and n-butyl reference patterns with an appropriate "weighting factor." The Marlex "base" pattern provided a low-level methyl (< 1/1000 CH₂) reference content, and the ethylene-butene and ethylene-hexene copolymers gave known fragmentation peaks due to ethyl- and n-butyl-branch content, respectively. These combinations resulted in an estimated branch content for NBS HDPE of ~1 methyl, 0.1 ethyl, and 0.3 n-butyl/1000 CH₂.

In a similar manner, the branch content of NBS LDPE was estimated with the computer simulation method. In this instance, the ethylene-hexene copolymer with 12.8 n-butyl/1000 CH₂ was used to provide a "base" pattern in the isoalkane region between C₁₁ and C₁₂, and a series of ethyl-related peaks was added to this pattern from the pyrogram of the ethylene-butene copolymer (12.8 ethyl/1000 CH₂). A small contribution from the Marlex 50 pattern was also included. This trial-and-error procedure gave the best match to the NBS LDPE pyrogram when ~8 to 10 n-butyl and 2 to 3 ethyl branches/1000 CH₂ were combined in the simulation (Fig. 5).

Further application was made to the reduced PVC (100°C) polymer. Here the PHGC data had indicated the possible presence of ethyl and n-butyl branches, while these data and the FTNMR results had shown a methyl-branch content of ~2 to 3 methyl/1000 CH₂. Figure 6 shows the patterns from two attempted combinations representing (a) ~2 methyl and 0.5 n-butyl/1000 CH₂ and (b) ~2 methyl, 0.3 n-butyl, and 0.1 ethyl/1000 CH₂. It is likely that additional trial-and-error variations could improve the match, but the estimated 2 methyl/1000 CH₂ with low-level n-butyl and ethyl contents (~0.3/1000 CH₂) appears realistic. The unidentified enhanced peak in the pattern is indicated by the * symbol, as in the other pyrograms of reduced PVC.

SUMMARY

It has been demonstrated that both high-resolution PHGC and ¹³C FTNMR studies are able to detect and reasonably quantify the

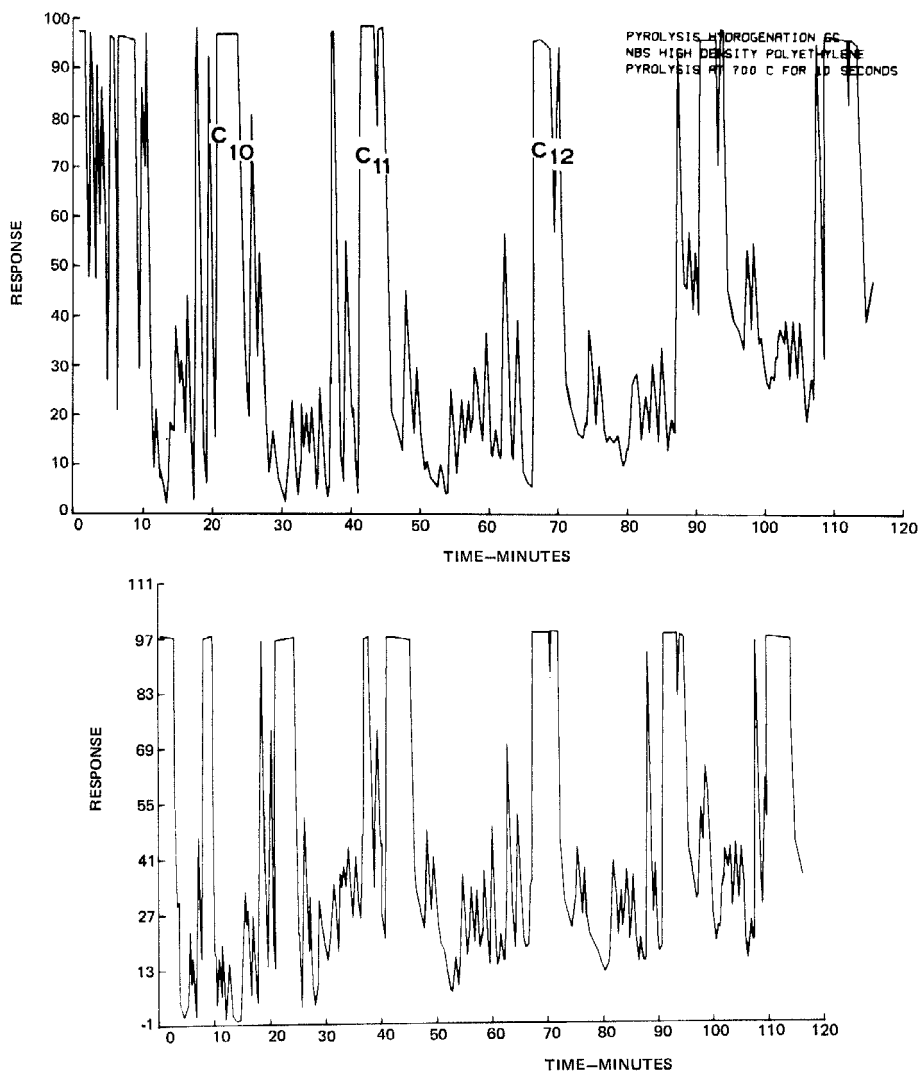


FIG. 4. Top, experimental pyrogram of NBS HDPE, digitized for simulation study; bottom, computer simulation of NBS HDPE pyrogram, using Marlex 50 "base" pattern and adding two copolymer reference patterns to it between C₁₁ and C₁₂.

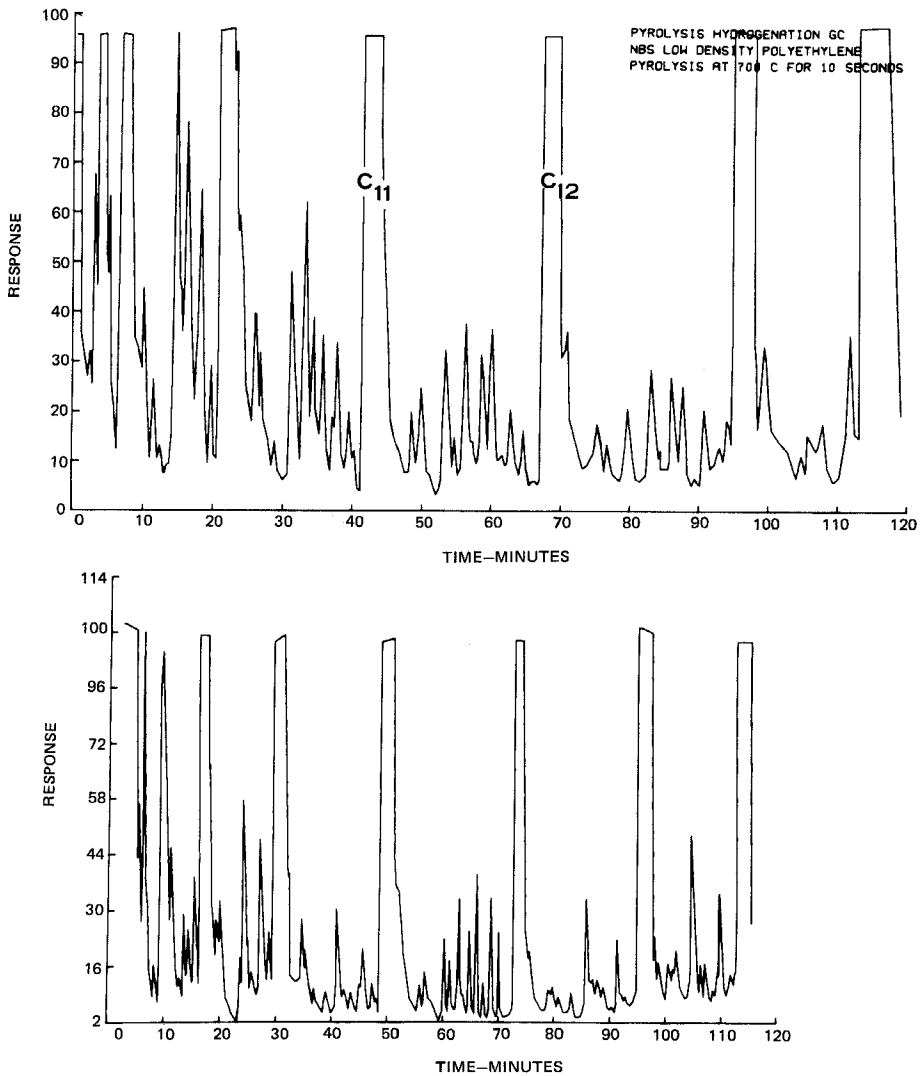


FIG. 5. Top, experimental pyrogram of NBS LDPE, digitized for simulation study; bottom, computer simulation of NBS LDPE pyrogram, using ethylene-hexene copolymer "base" pattern and adding Marlex 50 and ethylene-butene copolymer patterns to it between C₁₁ and C₁₂.

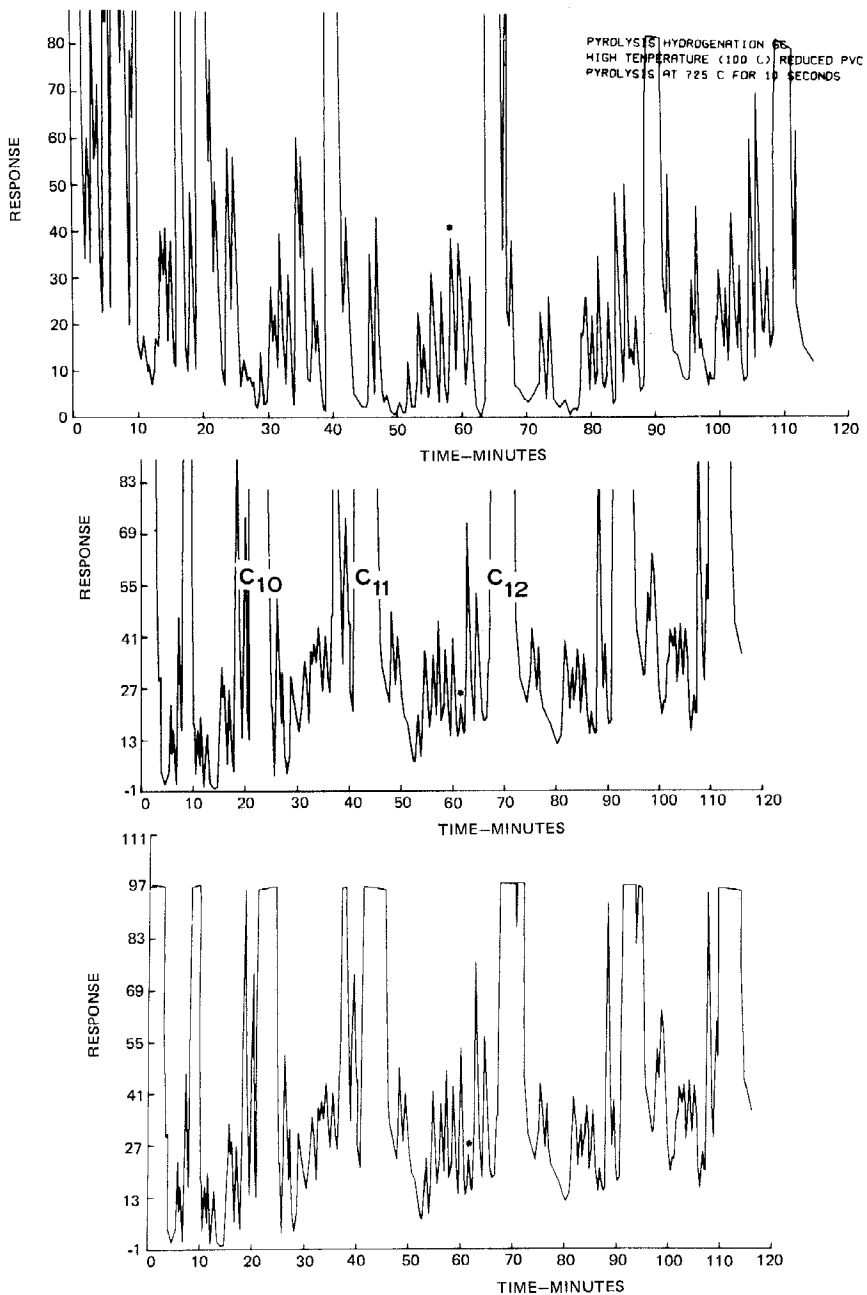


FIG. 6. Top, experimental pyrogram of high-temperature (100°C) reduced PVC, digitized for simulation study; center, computer simulation of high-temperature (100°C) reduced-PVC pyrogram, using Marlex 50 "base" pattern and adding an ethylene-hexene copolymer pattern to it

short-branch content in PE and reduced-PVC systems. The PHGC method would appear to be limited at this time, under our experimental conditions, to an inherent detection level of 1 methyl, ethyl, or n-butyl branch/1000 CH₂ along the polymer chain. A new computer program was developed to aid in interpreting minor changes in the types or relative amounts of branches, using known references to simulate isoalkane fragmentation patterns of the unknowns. This procedure allowed inferences to be made regarding the presence or absence of even lower branch contents; ~0.1/1000 CH₂ in the selected systems. Additionally, the detection of other structural defects may occur from the presence of extraneous peaks in the experimental fragmentation patterns. With the appropriate expenditure for suitable instrumentation, the ¹³C FTNMR method may be used to detect even lower levels of short-chain branches than those reported here. Clearly, both techniques provide significant information on polymer microstructure that is not otherwise readily obtained.

ACKNOWLEDGMENT

Aid by D. C. Messersmith (Armstrong) in developing the computer simulation program is gratefully acknowledged.

REFERENCES

- [1] D. H. Ahlstrom, S. A. Liebman, and K. B. Abbàs, J. Polym. Sci., Polym. Chem. Ed., **14**, 2479 (1976).
- [2] M. E. A. Cudby and A. Bunn, Polymer, **17**, 345 (1976).
- [3] M. A. McRae and W. F. Maddams, Makromol. Chem., **177**, 449 (1976); cf. C. Baker, P. David, and W. F. Maddams, Ibid., **180**, 975 (1979).
- [4] H. N. Cheng, F. C. Schilling, and F. A. Bovey, Macromolecules, **9**, 363 (1976).
- [5] F. A. Bovey, F. C. Schilling, F. L. McCrackin, and H. L. Wagner, Ibid., **9**, 76 (1976).
- [6] D. J. Cutler, P. J. Hendra, M. E. A. Cudby, and H. A. Willis, Polymer, **18**, 1005 (1977).
- [7] T. N. Bowmer and J. H. O'Donnell, Ibid., **18**, 1032 (1977).
- [8] D. E. Axelson, L. Mandelkern, and G. C. Levy, Macromolecules, **10**, 557 (1977).
- [9] D. E. Axelson, G. C. Levy, and L. Mandelkern, Ibid., **12**, 41 (1979).

FIG. 6 (continued) between C₁₁ and C₁₂; bottom, computer simulation of high-temperature (100°C) reduced-PVC pyrogram, using Marlex 50 "base" pattern and adding ethylene-butene and ethylene-hexene copolymer patterns to it between C₁₁ and C₁₂.

- [10] F. A. Bovey, F. C. Schilling, and W. H. Starnes, Jr., Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., **20**(2), 160 (1979).
- [11] Y. Sugimura and S. Tsuge, Macromolecules, **12**, 512 (1979).
- [12] R. Pétiand and Q.-T. Pham, Makromol. Chem., **178**, 741 (1977).
- [13] S. A. Liebman, D. H. Ahlstrom, and C. R. Foltz, J. Polym. Sci., Polym. Chem. Ed., **16**, 3139 (1978).
- [14] W. H. Starnes, Jr., R. L. Hartless, F. C. Schilling, and F. A. Bovey, Adv. Chem. Ser., **169**, 324 (1978); Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., **18**(1), 499 (1977).
- [15] W. H. Starnes, Jr., F. C. Schilling, K. B. Abbäs, I. M. Plitz, R. L. Hartless, and F. A. Bovey, Macromolecules, **12**, 13 (1979).
- [16] W. H. Starnes, Jr., F. C. Schilling, K. B. Abbäs, R. E. Cais, and F. A. Bovey, Ibid., **12**, 556 (1979).
- [17] U. Schwenk, F. Cavagna, F. Lömkker, I. König, and H. Streitberger, J. Appl. Polym. Sci., **23**, 1589 (1979).
- [18] W. H. Starnes, Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, D. J. Freed, R. L. Hartless, and F. A. Bovey, Manuscript in Preparation.
- [19] A. Nakajima, H. Hamada, and S. Hayashi, Makromol. Chem., **95**, 40 (1966).
- [20] A. Rigo, G. Palma, and G. Talamini, Ibid., **153**, 219 (1972).
- [21] M. D. Baijal, T. S. Wang, and R. M. Diller, J. Macromol. Sci.-Chem., **4**, 965 (1970).
- [22] E. M. Sorvik, J. Appl. Polym. Sci., **21**, 2769 (1977).
- [23] Unpublished work at Armstrong using a Digilab 10M FTIR spectrometer to analyze reduced-PVC samples and PE reference materials.
- [24] D. R. Rueda, F. J. Baltá Calleja, and A. Hidalgo, Spectrochim. Acta, Part A, **35**, 847 (1979).
- [25] N. L. Earl and D. L. VanderHart, Macromolecules, **12**, 762 (1979).
- [26] Nicolet Technology Corp., 145 E. Dana St., Mountain View, California 94041; Applications Booklet, NT-Series Fourier Transform Superconductive Magnet NMR Spectrometers, 1980, p. 18.
- [27] S. A. Liebman, D. H. Ahlstrom, and T. E. Roeser, Eastern Analytical Symposium, New York, November 1980.

Note Added in Proof. Carbon-13 FTNMR spectra obtained at a field strength of 50.31 MHz have now confirmed the presence of n-butyl branches in the reduced-PVC samples of the present study [W. H. Starnes, Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, and F. A. Bovey, Polym. Bull. (Berlin), **4**, 555 (1981)]. The 50.31-MHz spectra indicate the following concentrations ($\pm 0.1/1000 \text{ CH}_2$) for the completely reduced short-branch structures in these samples: 2.8 methyl, 0.6 ethyl, 1.0 n-butyl (polymer S-54); 2.0 methyl, 0.8 ethyl, 0.9 n-butyl (100°C polymer).