

The Characterization of Short Chain Branching in Polyethylene Using Fourier Transform Infrared Spectroscopy

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SYNOPSIS

The characterization of short chain branching in polyethylene using transmission FTIR spectroscopy is investigated. Traditional methodologies, using the methyl deformation band for qualitative and quantitative analyses, have recognized shortcomings. The methyl and methylene rocking bands, which are more characteristic of short chain branch type, were found to be more useful. Methyl, ethyl, butyl, isobutyl, and hexyl branches are qualitatively and quantitatively characterized in LLDPE copolymers by FTIR spectroscopy. Methyl branches were characterized by an absorbance at 935 cm^{-1} , ethyl branches at 770 cm^{-1} , butyl branches at 893 cm^{-1} , isobutyl branches at 920 cm^{-1} , and hexyl branches at 888 cm^{-1} . Fourier self-deconvolution was used to resolve overlapping bands for ethyl, butyl, and isobutyl branches. Using calibrations derived for LLDPE copolymers from ^{13}C NMR data, FTIR spectroscopy was also used to characterize LLDPE terpolymers and LDPE resins. The FTIR and NMR data are in qualitative and quantitative agreement. In some cases corrections were made to the FTIR results using data obtained from the methyl deformation band. The FTIR technique is less costly and faster than NMR spectroscopy.

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INTRODUCTION

Short chain branching in linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) affects many physical properties such as density, rigidity, hardness, permeability and environmental stress crack resistance.¹ Because of the commercial importance of these polymers, many workers have undertaken studies to investigate the role of short chain branching on physical properties.²⁻⁵ There are many important and complicated questions which remain unanswered; thus interest in this field remains strong.

The analysis of short chain branching in polyethylene is important for the correlation of molecular structure with physical properties. Although a variety of techniques have been used, only spectroscopic methods provide direct measurements of short chain branching. While infrared spectroscopy had been traditionally used, ^{13}C NMR spectroscopy

has been more commonly applied during the last 10 years because NMR can readily identify and quantify branch type (up to hexyl branches).⁶⁻¹³ The continuing use of infrared spectroscopy for short chain branching analysis is a direct consequence of simplicity, speed, and low equipment cost. As a practical matter, therefore, advances in infrared spectroscopic methods for the analysis of short chain branching in polyethylene are important.

The historical shortcomings of infrared spectroscopic measurements are readily apparent. Infrared spectroscopic methods for short chain branching in LDPE have focussed on the methyl deformation band at approximately 1378 cm^{-1} . The first quantitative method was reported in 1950¹⁴ which subsequently evolved into an ASTM standard method.¹⁵ As additional work was done using infrared spectroscopy for the characterization of LLDPE, which contains specific short chain branch types, limitations of the methyl deformation band became recognized. For instance, since the 1378 cm^{-1} band cannot differentiate short chain branches from end groups, at low branching levels correction factors must be used to separate the two.¹⁶ Additional com-

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plications result because the molar absorptivity of the methyl deformation band varies with short chain branch length¹⁷⁻¹⁹ and branch ends.¹² Recognizing these shortcomings, work has been done to correct for branch ends,¹⁶ and to investigate the possibility of using the 1378 cm^{-1} band as a qualitative tool.¹⁹⁻²¹ If branch type could be qualitatively analyzed, then calibrations for a particular branch type could be constructed from materials previously analyzed by ^{13}C NMR spectroscopy.¹⁷ This would solve the problem of varying molar absorptivity with branch type. Previous reports,¹⁹⁻²¹ and results described here, indicate that this approach is at best marginal.

Perhaps because it was recognized that the methyl deformation band is of limited use for characterization purposes, some workers have examined infrared spectra of LLDPE and LDPE resins for bands characteristic of a given branch type. These workers have focussed on the methyl rocking region between 1200 and 800 cm^{-1} , and the methylene rocking region between 770 and 720 cm^{-1} . McRae et al.²² and others¹⁹ have found a band at 935 cm^{-1} which is specific for methyl branches. McRae and Maddams²² have found this band to be quantitative for methyl branching determinations, after bromination of the sample, to eliminate an interfering band from terminal vinyl unsaturation at 910 cm^{-1} .²³ Rugg et al.²⁴ and Willbourn²⁵ were the first to observe an absorbance at 770 cm^{-1} attributable to the methylene rocking mode of ethyl branches. Although Willbourn looked at the 770 cm^{-1} band semiquantitatively,²⁵ this work has received very little attention.¹⁹ The 770 cm^{-1} peak is a small shoulder of the large 730 cm^{-1} absorbance from the crystalline portion of polyethylene,²⁶ thus limiting its usefulness for characterization purposes. Previous workers have also shown^{19,22,27} that a methyl rocking band at 890 cm^{-1} exists for butyl and longer branches. Work by Usami and Takayama suggested¹⁹ that butyl branches can be differentiated from hexyl and longer branches, since they reported a 4 cm^{-1} shift between the two branch types. Finally, Tosi et al.²⁸ and Maddams and Woolmington²⁷ discuss a methyl rocking band for isobutyl branches at 920 cm^{-1} .

Although this field has received some attention, little quantitative data has been reported for the analysis of short chain branching in polyethylene using the methyl and methylene rocking bands. Since FTIR spectroscopy is a relatively simple, fast, and potentially quantitative approach, we have undertaken a study to investigate the use of this technique for the qualitative and quantitative determination of short chain branching in polyethylene. In this paper we report FTIR calibrations for methyl,

ethyl, butyl, hexyl, and isobutyl branching in LLDPE copolymers based on ^{13}C NMR values. These calibrations are then applied to the analysis of short chain branching in LLDPE terpolymers and conventional LDPE. The FTIR results are compared to data obtained by ^{13}C NMR spectroscopy of the same polymers.

EXPERIMENTAL

Materials

Polyethylene samples originated from a variety of sources. All LLDPE copolymer samples were separated from additives prior to analysis by dissolving in boiling toluene (approximately 2 g of sample in 200 mL of toluene) for 30 min. The polymers were cooled to room temperature and excess acetone added to the solution. After precipitation the polymers were filtered through a medium porosity sintered glass funnel. The polymers were then vacuum dried at 40°C for 16 h. LLDPE terpolymers and LDPE resins were analyzed as received with additives present.

Characterization

Samples were prepared for FTIR spectroscopy by hot pressing approximately 100 mg of polymer between polyester sheets in a mold, at temperatures in the range of 110–160°C, depending on the melting point of the polymer. Samples were pressed for approximately 60 s at 2000 psi, immediately removed from the press, and air-cooled to ambient temperature. Film thicknesses were measured in four places where the infrared beam transmits through the polymer. Thicknesses used were the mean of the four measurements. For methyl deformation band measurements, films were typically 0.1 mm thick. For measurements in the methyl and methylene rocking mode regions, films were typically 0.3–0.4 mm thick.

Infrared spectra were acquired using a Nicolet 60SX FTIR spectrometer purged with dry nitrogen and equipped with a DTGS detector. Typically 128 scans were signal averaged at 2 cm^{-1} nominal resolution using Happ–Genzel apodization and one level of zero filling. Spectra were also acquired at 0.2 cm^{-1} nominal resolution using a narrow band MCT detector (all other parameters remaining unchanged), to obtain methyl deformation band position measurements. Band area and position measurements were obtained using standard Nicolet software.

To enhance the analytical usefulness of many of the bands used for short chain branching analysis, Fourier self-deconvolution was used to mathematically resolve overlapping bands. This technique makes some analyses possible and others easier by obviating the need for bromination to eliminate interfering vinyl group unsaturation peaks. The method used is similar to that described by Kauppinen et al.,²⁹ and graciously supplied by Nicolet instruments. In all cases since² apodization was used, only halfwidth and K -values were varied. For methyl deformation band position measurements, halfwidth = 5, K -value = 2. For methyl deformation band area measurements, halfwidth = 7, K -value = 2. For the methylene rocking band at 770 cm^{-1} , halfwidth = 20 and K -value = 1.5. For the methyl rocking mode of butyl branches, halfwidth = 12 and K -value = 1.3. Finally for the methyl rocking band of isobutyl branches, halfwidth = 8 and K -value = 1.5.

Sample preparation for NMR analysis consisted of dissolving 0.2 g of polymer in 1.3 mL of a 1,2,4-trichlorobenzene/benzene- d_6 (4 : 1) solution. The mixture was heated to 125°C for approximately 2–4 h with frequent agitation or until the solution appeared homogeneous.

NMR analyses were conducted on a Varian Unity-300 spectrometer operating at 75.4 MHz for ^{13}C . The results were obtained at 125°C , using an acquisition time of 3.0 s and a sweepwidth of 14,000 Hz. An observe pulsewidth of $18\text{ }\mu\text{s}$ ($\pi/2$) was used with a 15 s recycle delay time. The proton decoupler remained on for the complete cycle. The data was processed using 1 Hz of line broadening and baseline correction in all instances.

The number of branches per 1000 total carbons was determined from the appropriate integral regions. Accurate branching levels could be calculated using resonances with sufficiently short relaxation times. For LLDPE copolymer and terpolymer branching determinations, resonances with spin lattice relaxation times of less than 3.5 s were used. For LDPE resins, the signal overlap in the methine region (37–40 ppm) and the alpha methine regions (33–36 ppm) required that single specific resonances be used to determine branching levels. For the LDPE resin containing methyl side chains, the number of branches was determined from the methine resonance at 33.3 ppm, which in this instance was adequately resolved. Ethyl branching in LDPE resins was determined from the methyl resonance at 11 ppm. The T_1 for this signal was estimated to be 6.4 s, indicating that only 94% of the magnetization had recovered during the 18 s delay between pulses. In

this case the resonance was increased by a factor of 1.06 in order to obtain quantitative results. The butyl branching determination was obtained from the signal at 23.4 ppm ($T_1 = 4.2\text{ s}$) with a 1.02 scaling factor applied to this signal. The number of amyl branches and longer were obtained from the signal at 22.8 ppm ($T_1 = 6.2\text{ s}$) with a scaling factor of 1.08.

RESULTS AND DISCUSSION

Linear Low Density Copolymers

The set of linear low density copolymers studied are shown in Table I. Investigations of the use of the methyl deformation band for qualitative and quantitative analyses of short chain branching were undertaken. It has been previously found that the molar absorptivity of the methyl deformation band decreases with increasing branch length.¹⁹ Our data support these conclusions but provide no additional information, so that no further discussion of the data

Table I Data for LLDPE Copolymers

Branch Type	Branch Content	Me Deformation Band Position	Me Rocking Band Position
Methyl	3	1377.09	935
Methyl	21	1377.13	935
Methyl	24	1377.14	935
Methyl	33	1377.25	935
Ethyl	5	1379.05	886.9 ^a
Ethyl	11	1378.76	887.1 ^a
Ethyl	17	1379.11	887.2 ^a
Ethyl	21	1379.14	886.8 ^a
Ethyl	28	1379.16	886.9 ^a
Butyl	8	1377.74	893.2
Butyl	11	1377.75	893.8
Butyl	15	1377.78	894.2
Butyl	16	1377.79	894.0
Hexyl	3	1377.61	888.6
Hexyl	7	1377.60	889.2
Hexyl	13	1377.72	889.1
Hexyl	18	1377.69	889.1
Hexyl	22	1377.71	889.0
Isobutyl	5	1383.20	920
Isobutyl	7	1383.22	920
Isobutyl	8	1383.19	920
Isobutyl	10	1383.20	920
Isobutyl	11	1383.21	920
Isobutyl	17	1383.20	920
Isobutyl	22	1383.23	920

^a Interfering absorbance from end groups and/or *trans*-vinylidenes.

will be made here. However, using the polymers shown in Table I, high resolution spectra to precisely determine methyl deformation band position provides a more complete set of data compared to previous reports.¹⁹⁻²¹ Inspection of the methyl deformation band position (Table I) shows that ethyl and isobutyl branches are readily distinguishable from the other branch types. There is a greater than 1 cm^{-1} shift between ethyl and isobutyl branches from the other branch types, whereas the reproducibility of the peak position measurement was found to be better than 0.1 cm^{-1} . With this high level of precision, it is also possible to differentiate methyl branches using the band position. Distinguishing butyl and hexyl branches using the methyl deformation band is not currently possible. Previous workers have reached similar conclusions.²¹

Maddams and Parker²¹ reported approximately a 1 cm^{-1} shift in methyl deformation band position with constant branch type and increased branch content. They suggested that the peak position of methyl groups in the crystalline region are at slightly lower frequency than the peak position for methyl groups in the amorphous region. Although the data in Table I shows the same trend (peak position shifting to higher frequency with increased branch content), we find these shifts are $0.1\text{--}0.2\text{ cm}^{-1}$. These shifts are very small and somewhat polymer-dependent. It is thus very difficult to assign the band shifts to a particular structural feature.

This discussion highlights some drawbacks concerning the usefulness of the methyl deformation band for characterization purposes. While previous workers have also recognized this and identified absorbances attributable to certain branch types,^{19,22,27} quantitative studies have not to our knowledge been

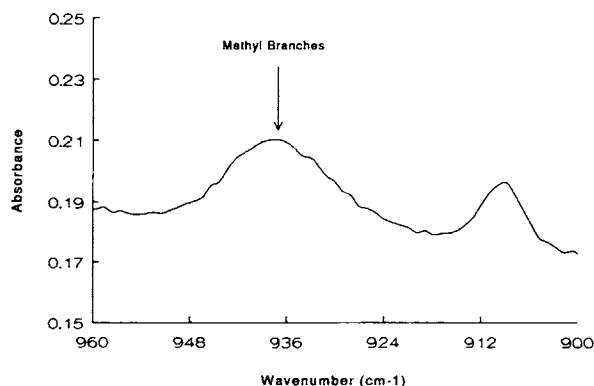


Figure 1 FTIR spectrum of an ethylene/propylene copolymer containing approximately 20 methyl branches/1000C.

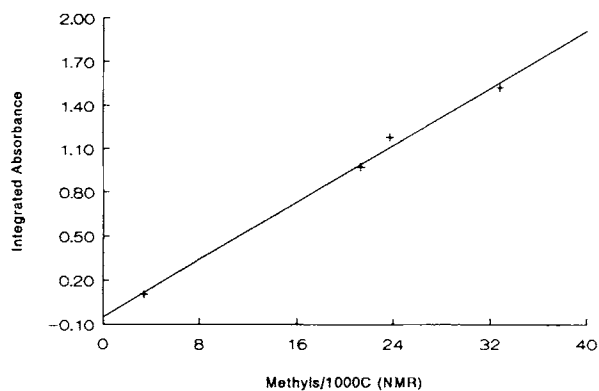


Figure 2 Calibration for methyl branching using 935 cm^{-1} absorption.

reported. As Table I indicates, a relatively complete set of LLDPE copolymers has been compiled for this study. This makes quantitative investigations possible.

As previously discussed, McRae and Maddams²² used an absorbance at 935 cm^{-1} to quantitate methyl branching after bromination to eliminate a band from terminal vinyl unsaturation (910 cm^{-1}). The infrared spectrum of an ethylene/propylene copolymer is shown in Figure 1. At this resolution (2 cm^{-1}) no interference from the terminal vinyl unsaturation band is seen, thus obviating the need for bromination or deconvolution. Spectra of the series of ethylene/propylene copolymers shown in Table I were obtained, and the 935 cm^{-1} absorbance was integrated. The resulting calibration line is shown in Figure 2. Since no other polyethylene bands absorb at 935 cm^{-1} , this absorbance is useful for both qualitative and quantitative analyses of ethylene/propylene copolymers.

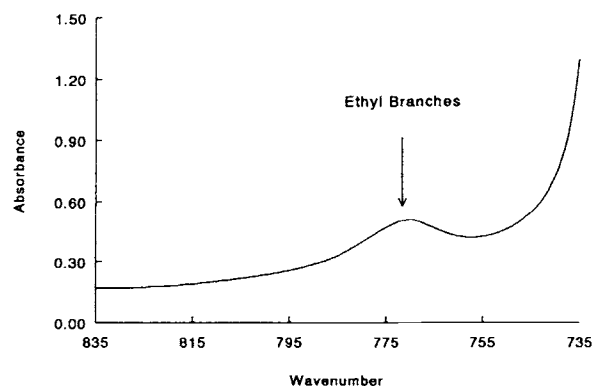


Figure 3 FTIR spectrum of an ethylene/1-butene copolymer containing approximately 30 ethyl branches/1000C.

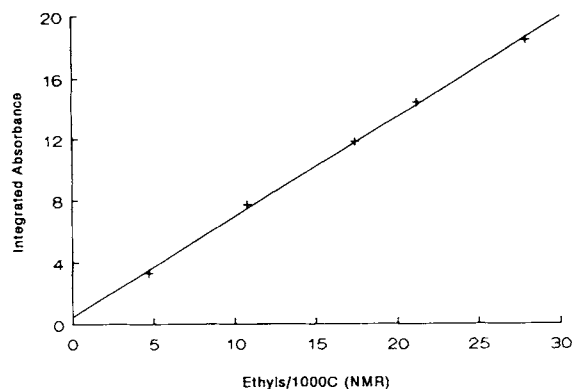


Figure 4 Calibration for ethyl branching using 770 cm^{-1} absorption.

An absorbance attributable to ethyl branches has been previously identified at 770 cm^{-1} .^{24,25} In Figure 3, a spectrum of an LLDPE containing ethyl branches is shown. This band rests on the side of a strong band at 730 cm^{-1} . To our knowledge, successful quantitative data using the 770 cm^{-1} absorbance has not been reported. Using Fourier self-deconvolution to mathematically resolve the 770 cm^{-1} absorbance from the 730 cm^{-1} band, followed by integration, the calibration line shown in Figure 4 was obtained. This suggests that ethyl branches can be quantitatively analyzed using deconvolution and the 770 cm^{-1} band.

A band at approximately 890 cm^{-1} has been assigned to a methyl rocking mode for branches larger than ethyl.^{19,22,27} A series of polyethylenes with varying amounts of butyl branches were obtained with spectra (normalized to film thickness) shown in Figure 5. These spectra illustrate the significant overlap between the 910 cm^{-1} terminal vinyl unsaturation band and the 890 cm^{-1} band predominantly

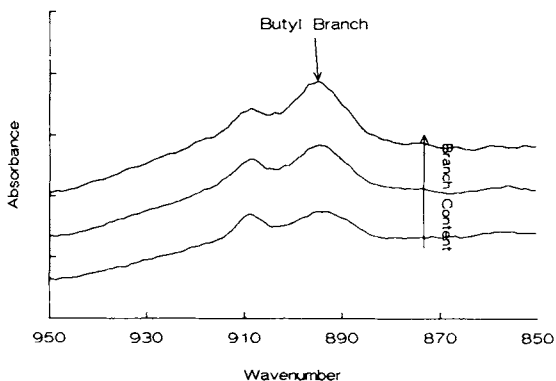


Figure 5 FTIR spectra of ethylene/1-hexene copolymers.

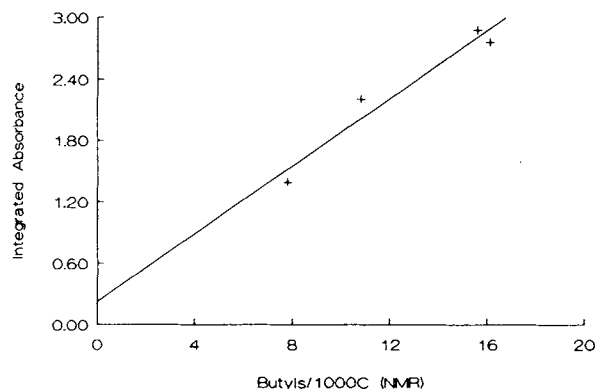


Figure 6 Calibration for butyl branching using 893 cm^{-1} absorption.

from butyl branches, making deconvolution necessary. Spectral subtraction is not viable since different polymers containing varying amounts of unsaturation makes it impossible to reliably subtract the 910 cm^{-1} band. After Fourier self-deconvolution, the data was quantitatively analyzed. The resulting calibration line shown in Figure 6 indicates that the 890 cm^{-1} band can be used as a quantitative measure of butyl branching in polyethylene.

In Figure 7, spectra of a series of octene-modified polyethylenes are shown (normalized to film thickness). The 910 cm^{-1} band is resolved from the 890 cm^{-1} band from hexyl branches, so that the 890 cm^{-1} band can be integrated directly. Upon analyzing data for hexyl branching quantitatively, the linear relationship shown in Figure 8 is obtained. The data suggests that the 890 cm^{-1} band can be used as a quantitative measure of hexyl branching in polyethylene.

The discussion thus far has not suggested how to differentiate butyl from hexyl branches. Following

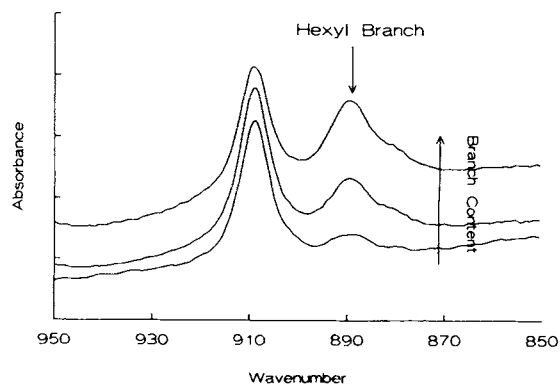


Figure 7 FTIR spectra of ethylene/1-octene copolymers.

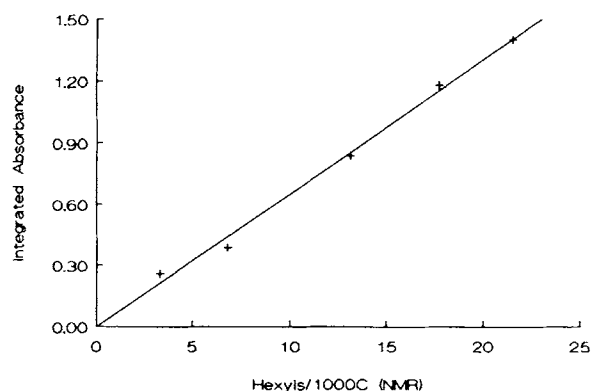


Figure 8 Calibration for hexyl branching using 888 cm^{-1} absorption.

the lead of others,¹⁹ we have confirmed a 5 cm^{-1} shift in the methyl rocking band position for butyl and hexyl branches (Table I). Thus the position of this band can be used to qualitatively differentiate between butyl and hexyl branch types. There is also approximately a 2 cm^{-1} shift between the position noted for ethyl and butyl branched polymers. The band detected for the ethyl branched polymers is not attributable to ethyl groups, however, since the band area was independent of branch content. This band may be attributable to endgroups and/or *trans*-vinylidene unsaturation.²³ It should be noted that (1) the affect of saturated endgroups on the quantitative analysis of butyl and hexyl branches may be significant for low molecular weight polymers and (2) polymers with large concentrations of *trans*-vinylidene species may also affect these analyses.

Isobutyl branches are readily identifiable by a band at 920 cm^{-1} .^{27,28} While we have found that use of the 920 cm^{-1} band after deconvolution can yield quantitative data (not shown), from a characterization standpoint the more commonly used methyl

deformation band is very diagnostic for isobutyl branches (Table I). Since isobutyl branches are readily analyzed using the methyl deformation band, and 4-methylpentene copolymers of ethylene are less common, this copolymer system will not be discussed further.

Results presented in this section suggest short chain branching type and content in LLDPE copolymers can be rapidly and quantitatively analyzed using conventional FTIR techniques. These characterization methods will next be applied to more complex LLDPE terpolymers and conventional LDPE as a test of the applicability of the technique.

Linear Low Density Terpolymers

Having identified bands and developed quantitative protocols for the analysis of various short chain branching types in LLDPE, the applicability of these techniques can be tested with terpolymer systems. Four different terpolymers were analyzed by NMR and FTIR spectroscopies. A comparison of results from the two techniques is shown in Table II. Short chain branch types are readily identified by FTIR spectroscopy, thus qualitatively identifying terpolymer type. The quantitative branch content data obtained by FTIR spectroscopy is satisfactory, although the ethyl branching content data has a larger error than expected. These data show that it is possible to rapidly analyze short chain branching type and content in LLDPE with more than one kind of short chain branch using FTIR spectroscopy.

Low Density Polyethylene

The applicability of FTIR spectroscopy to analyze short chain branching in high pressure low density polyethylene which contain several different branch

Table II Comparison of FTIR and NMR Results for Short Chain Branching Analysis of LLDPE Terpolymers

	Me Branches/1000C	Et Branches/1000C	Butyl Branches/1000C
FTIR data	0	11	9
NMR data	0	8	10
FTIR data	0	16	5
NMR data	0	14	6
FTIR data	19	4	0
NMR data	18	6	0
FTIR data	0	14	11
NMR data	0	11	10

Table III Comparison of FTIR and NMR Results for Short Chain Branching Analysis of LDPE Resins

		Me/1000C	Et/1000C	Bu+/1000C	Am+/1000C	Total	CH ₃ /1000C	Bu/ 1000C Corrected	Total Corrected
LDPE-1	FTIR	2	3	15 ^a	—	20	19	15 ^a	20
LDPE-1	NMR	3	3	6	5	17	—	—	—
LDPE-2	FTIR	0	0	17 ^a	—	17	19	17 ^a	17
LDPE-2	NMR	0	3	7	5	15	—	—	—
LDPE-3	FTIR	0	2	31 ^a	—	33	20	18 ^a	20
LDPE-3	NMR	0	5	9	7	21	—	—	—
LDPE-4	FTIR	1	6	31 ^a	—	38	23	16 ^a	23
LDPE-4	NMR	0	6	9	6	21	—	—	—
LDPE-5	FTIR	0	4	28 ^a	—	32	17	13 ^a	17
LDPE-5	NMR	0	0	14	3	17	—	—	—

^a Butyl and longer branches.

types was also explored. Five LDPE resins were analyzed by NMR and FTIR spectroscopies; results are shown in Table III. The data obtained by FTIR and NMR are in qualitative agreement. FTIR spectroscopy cannot qualitatively differentiate butyl from hexyl branches when both are present, whereas NMR spectroscopy can. For three of the LDPE resins, the FTIR data for butyl and longer branches is significantly higher than that obtained by NMR. It is speculated that this may be caused by interferences from high concentrations of *trans*-vinylidene species, which also absorb in the 890 cm⁻¹ region.²³ Relatively high concentrations of *trans*-vinylidene in LDPE (compared to LLDPE) are not uncommon.

When interferences in the branching analyses occur, additional data work up using the methyl deformation band is necessary. The total number of methyl, ethyl, and butyl and longer branches should approximately equal the methyl/1000C number obtained using the deformation band at approximately 1378 cm⁻¹. If the two numbers approximately match (LDPE 1 and 2), then it is assumed that there are no interferences. If, on the other hand, the total number of individual branch types measured far exceeds that obtained using the methyl deformation band, then it is assumed that the band at 890 cm⁻¹ measuring butyl and longer branches has interferences (LDPE 3-5). In these cases corrections were made to the data. The difference between the total individual branching number and the number obtained from the methyl deformation band was subtracted from the butyl and larger branching number. This corrected value is much closer to the data obtained by NMR spectroscopy, as shown in Table III.

It is thus possible to qualitatively and quantitatively analyze for short chain branching in LDPE using FTIR spectroscopy.

CONCLUSIONS

Applying conventional transmission FTIR spectroscopy, it is possible to rapidly and easily analyze methyl, ethyl, butyl, hexyl, and isobutyl branching in LLDPE copolymers. The applicability of FTIR to characterize short chain branching in LLDPE terpolymers and LDPE was also explored. Ethene/propene/butene and ethene/butene/hexene terpolymers were successfully analyzed. When butyl and hexyl branches are simultaneously present, they cannot be differentiated. Methyl, ethyl, and butyl and longer branching data have been obtained using FTIR spectroscopy of LDPE. The methods described in this report make FTIR spectroscopy much more powerful for the characterization of short chain branching in polyethylenes and provide a rapid, inexpensive alternative to NMR spectroscopy for these analyses.

We thank Ian Peat, Mani Shanker, Dave Bailey, and Quantum Chemical Corporation for supporting and allowing us to publish this work. We also thank Evan Church for providing the terpolymers, and Amy Galbraith for performing many of the analyses.

REFERENCES

1. K. Shirayama, S. Kita, and H. Watabe, *Makromol. Chem.*, **151**, 97 (1972).

2. R. Alamo, R. Domszy, and L. Mandelkern, *J. Phys. Chem.*, **88**, 6587 (1984).
3. J. Ross, *J. Macromol. Sci. Pure Appl. Chem.*, **A29**, 65 (1992).
4. E. Karboshewi, L. Kale, A. Rudin, W. Tchir, and J. Pronovost, *J. Appl. Polym. Sci.*, **44**, 425 (1992).
5. R. Ford, *J. Appl. Polym. Sci.*, **9**, 2879 (1965).
6. M. DePooter, P. Smith, K. Dohrer, K. Bennet, M. Meadows, C. Smith, H. Schouwenaus, and R. Geerards, *J. Appl. Polym. Sci.*, **42**, 399 (1991).
7. J. Randall, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **C29**, 201 (1989).
8. J. Randall and E. Hsieh, *NMR and Macromolecules*, ACS Symposium Series 247, J. Randall, Ed., Am. Chem. Soc., Washington, D.C., 1984, Chap. 9.
9. J. Randall, *Polymer Characterization by ESR and NMR*, ACS Symposium Series 142, A. Woodward and F. A. Bovey, Eds, Am. Chem. Soc., Washington, DC, 1980.
10. H. Cheng, *Macromolecules*, **24**, 4813 (1991).
11. D. Grant and E. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
12. L. Lindeman and J. Adams, *Anal. Chem.*, **43**, 1245 (1971).
13. C. Carman, A. Tarpley, Jr., and J. Goldestein, *Macromolecules*, **6**, 719 (1973).
14. L. Cross, R. Richards, and H. Willis, *Discuss. Faraday Soc.*, **9**, 235 (1950).
15. American Society for Testing Materials Designation D2238 (1968).
16. C. Baker and W. Maddams, *Makromol. Chem.*, **177**, 437 (1976).
17. W. Maddams, D. Morris, and H. Willis, *Polym. Commun.*, **30**, 180 (1989).
18. C. Baker, W. Maddams, G. Park, and B. Robertson, *Makromol. Chem.*, **165**, 321 (1973).
19. T. Usami and S. Takayama, *Polym. J.*, **16**, 731 (1984).
20. G. Muller, E. Schroder, and J. Osterode, *Acta Polym.*, **32**, 270 (1981).
21. W. Maddams and S. Parker, *Makromol. Chem.*, **189**, 333 (1988).
22. M. McRae and W. Maddams, *Makromol. Chem.*, **177**, 449 (1976).
23. E. Cernia, C. Mancini, and G. Montavdo, *Polym. Lett.*, **1**, 371 (1963).
24. F. Rugg, J. Smith, and L. Waterman, *J. Polym. Sci.*, **11**, 1 (1953).
25. A. Willbourn, *J. Polym. Sci.*, **34**, 569 (1959).
26. R. Snyder, *Methods of Experimental Physics*, L. Marton and C. Marton, Eds., Academic, New York, 1980.
27. W. Maddams and J. Woolmington, *Makromol. Chem.*, **186**, 1665 (1985).
28. C. Tosi, M. Lachi, and A. Pinto, *Makromol. Chem.*, **120**, 225 (1968).
29. J. Kauppinen, D. Moffatt, H. Mantsch, and D. Cameron, *Appl. Spectrosc.*, **35**, 271 (1981).

Received April 15, 1993

Accepted June 11, 1993