Conclusions

Mild alkaline hydrolysis, such as used in our normal procedures, produces anionic polymer with the anionic sites well spaced along the polymer chain. Thus, these products are suitable for detailed studies on polymer interactions with clays as an example of one type of microstructure. High ionic strength during alkaline hydrolysis, however, significantly moderates the electrostatic effect of anionic sites on neighboring hydrolysis sites. Strong acid hydrolysis, on the other hand, tends to develop blocks of anionic sites. A combination of these factors suggests that conditions may exist for controlled generation of blocks of anionic sites along the polymer chain. It appears necessary to minimize imide formation during this process.

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Determination of Branches in Terpolymers of Ethylene, 1-Butene, and Long α-Olefin by Pyrolysis–Hydrogenation–Gas Chromatography

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ABSTRACT: Pyrolysis–hydrogenation–gas chromatography (PHGC) was applied to determine the branches in ethylene–1-butene–α-olefin terpolymers, where α-olefin was 1-decene, 1-dodecene, or 1-hexadecene. The polymers were prepared by using Ziegler–Natta catalysts in *n*-heptane suspension. Each branch type was identified from the characteristic methylalkane peak caused by β-scission of the branched carbon. Quantitative determinations were done by using ethylene–α-olefin copolymers as reference. Octyl, decyl, and tetradecyl branches were identified from the pyrograms. Branch contents determined by the PHGC technique were compared with those obtained by IR and ^{13}C NMR spectroscopy. Few scissions were observed in the branches of the copolymers.

Introduction

The length and distribution of branches have a substantial effect on the properties of polyethylene. Melt properties and solution viscosity are predominantly affected by long-chain branches, whereas crystallinity, density, crystalline melting temperature, stiffness, hardness, gas permeability, and chemical resistivity are related to short-chain branches.[1-3] In order to regulate polyethylene properties, it is important to produce branches under controlled circumstances, analyzing their concentrations and distributions. Coordination polymerization permits the production of desired branches using α-olefins as comonomers. α-Olefins containing 4–8 carbon atoms are commonly used commercially, though it is possible to use longer α-olefins. IR[4-6] spectroscopy and ^{13}C NMR[7-19] spectroscopy are generally the applied methods for characterization of chain branching in polyethylene. These methods are limited, however. For example, total branch content can reliably be measured by IR spectroscopy, but it cannot be used for characterization of different branch types. Ethylene–α-olefin copolymers prepared with known α-olefins have been widely studied by ^{13}C NMR spectroscopy[7,8,11,13,14] and the results applied to the determination of LDPE branches.[4,7,8,10,12-16] Branches from methyl to amyl can be measured individually by ^{13}C NMR spectroscopy, though branches of six or more carbon atoms cannot be differentiated. The quantitative analysis can be done from peak intensities of typical carbon atoms for different branches.[17-19]

Recently, pyrolysis–hydrogenation–gas chromatography (PHGC) has become a useful complement to IR and ^{13}C NMR spectroscopy for the characterization of poly-

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ethylene.[20-25] Many of PHGC's possibilities remain unexamined. In their comprehensive study, Seeger et al.[20] proved that yield and distribution of isoalkanes formed in the pyrolysis of polyethylene are extremely sensitive to the ethylene polymerization process. Scission from the α- and β-positions to the branched carbon atom has a higher probability than other scissions in polyethylene. Cleavage of the carbon–carbon bond in the polymer backbone of the branch site (α-scission) leads to the formation of n-alkanes after hydrogenation:

$$\mathrm{RCH_2CHR'CH_2R''} \xrightarrow[-\mathrm{RH}]{\mathrm{R}\cdot} \mathrm{RCH_2\dot{C}R'CH_2R''} \xrightarrow[-\cdot\mathrm{CH_2R}]{\alpha\text{-scission}} \mathrm{RCH{=}CHR'} \xrightarrow{\mathrm{Pd/H_2}} \mathrm{RCH_2CH_2R'} \quad (1)$$

Backbone cleavage at bond β to the branch site (β-scission) gives methylalkanes after hydrogenation:

$$\mathrm{RCH_2\dot{C}R'CH_2R''} \xrightarrow[-\cdot\mathrm{R''}]{\beta\text{-scission}} \mathrm{RCH_2CR'{=}CH_2} \xrightarrow{\mathrm{Pd/H_2}} \mathrm{RCH_2CHR'CH_3} \quad (2)$$

Because every branch type exhibits its own characteristic methylalkane peaks in PHGC, pyrograms can be used for the determination of the branches in polyethylene.

PHGC has been applied to the determination of short-chain branching in polyethylene.[23-25] This study examines whether PHGC can be used to determine branches longer than five carbons. Branch contents of three ethylene–1-butene–α-olefin terpolymers (α-olefin = 1-decene, 1-dodecene, or 1-hexadecene) were determined by using model ethylene–α-olefin copolymers with known branch contents for comparison. PHGC results were compared with those obtained by IR and ^{13}C NMR spectroscopy.

Experimental Section

Sample Preparation. A series of samples was prepared by suspension polymerization with Ziegler–Natta catalysts. Polymerizations were carried out in a 4 dm^3 semibatch stirred tank reactor; the reaction medium was n-heptane. Comonomers, catalysts, and hydrogen were fed to the reactor at the beginning of the polymerization. As comonomers 1-decene, 1-dodecene, and 1-hexadecene were used alone or with 1-butene. Reactor pressure was maintained with a continuous ethylene feed.

The catalyst was commercial aluminium-activated TiCl$_3$, the cocatalyst was Et$_3$Al, and the Ti/Al molar ratio was 0.5. Polymerization temperatures were in the range 80–90 °C and ethylene partial pressure was 700 kPa. The molecular weight of the polymers was regulated by hydrogen, the partial pressure of which was 300 kPa. After 2 h of polymerization, the reactor pressure was reduced. The reactor was cooled and the polymer slurry removed. The polymer was filtered and washed to remove catalyst residuals and then dried.

PHGC Analysis. A pyrolyzer (Chemical Data Systems Pyroprobe 120) was directly attached to a gas chromatograph (Carblo Erba Fractovap 2900) with a fused-silica capillary column (50 m × 0.25-mm i.d.) coated with SE-52 stationary phase and FID. The injection port liner was packed with the hydrogenation catalyst (2% Pd in Chromosorb P 80–100 mesh) and maintained at 250 °C. To protect the capillary column from tarry degradation products, an aluminum tube (15 cm × 3 mm) was inserted between the injector and the column. This tube was changed as needed.

Sample weights were 0.3–0.9 mg. Before pyrolysis, volatiles were desorbed from the samples by holding the pyrolyzer interface at 200 °C for 10 min. Hydrogen was used as a carrier gas at a flow rate of 65 cm^3/min at the pyrolyzer. After splitting by 1:50, the flow rate in the capillary column was 1.3 cm^3/min. After the pyroprobe coil was heated to 800 °C for 10 s, the hydrogenated degradation products were passed directly into the column. Column temperature was held at 50 °C for 5 min and then increased to 270 °C at a rate of 2 °C/min. The GC was connected to an HP-3353 E system so that peak areas and retention times were obtained automatically from each pyrogram.

IR Analysis. For the spectroscopic study, each sample was pressed into thin films (0.1–0.2 mm). The spectra were recorded with a double-beam IR spectrometer (Perkin-Elmer 683) equipped with a data station and microprocessor. The total methyl contents in the samples and model ethylene–α-olefin copolymers were determined from the absorption band at 1378 cm^{-1}. For the study of this region, the Perkin-Elmer SNGLE computer program was applied, using five standard LDPE samples with known CH$_3$/1000 C values for calibration.

^{13}C Analysis. The determination of the side-chain concentrations by ^{13}C NMR spectroscopy was possible because a single long α-olefin was used as comonomer in each prepared sample. Spectra were run on a JEOL FX 90 Q pulse Fourier transform spectrometer. Samples were 20 wt % solutions in trichlorobenzene at 160 °C. Broad-band noise decoupling was employed. Instrumental conditions were as follows: pulse width 45°, pulse repetition 3 s, spectral width 3000 Hz, number of scans 3000–10 000.

The peaks in the spectra of ethylene–1-butene–long α-olefin terpolymers were identified from the chemical shifts at 39.7, 34.1, 30.4, 27.3, 26.7, and 11.2 ppm relative to (CH$_3$)$_4$Si (typical for ethylene–1-butene copolymers) and shifts at 38.3, 34.6, 32.2, 30.4, 27.3, 22.8, and 14.1 ppm relative to (CH$_3$)$_4$Si (typical for copolymers of ethylene with long α-olefins).

Results and Discussion

Identification of Branches. The pyrogram of an ethylene–1-butene copolymer (Figure 1a) was obtained by the pyrolysis–hydrogenation method. Characteristic peaks are 3-methylalkanes formed from β-scissions in the backbone. Pyrograms b–d (Figure 1) are pyrograms of ethylene–1-butene–1-decene, ethylene–1-butene–1-dodecene, and ethylene–1-butene–1-hexadecene terpolymers. By comparing these pyrograms to the pyrogram in Figure 1a, one can observe that there are certain isoalkane peaks in addition to 3-methylalkanes, which must be characteristic peaks for octyl, decyl, or tetradecyl branches.

The characteristic isoalkane peaks for the octyl branch (2MC$_{10}$, 3MC$_{11}$, 4MC$_{12}$, etc.) are caused by β-scission in the backbone. This can also be observed in the pyrogram as growing intensities of these peaks (Figure 1b). Respectively, the characteristic peaks for the decyl branch are 2MC$_{12}$, 3MC$_{13}$, 4MC$_{14}$, etc. and 2MC$_{16}$, 3MC$_{17}$, 4MC$_{18}$, etc. for the tetradecyl branch. According to two β-scissions from the tertiary carbon, it is clear that the intensities of 2-methylalkanes are higher than those of 3-methylalkanes, 4-methylalkanes, etc. Thus, the existence of octyl, decyl, and tetradecyl branches can be observed without any difficulty in pyrograms, at least in the presence of ethyl branches.

Determination of Branch Content. In the pyrolysis of polyethylene, secondary reaction products (cyclic and branched hydrocarbons) are also formed. According to Seeger et al.,[20] these could result from secondary reactions such as intra- or intermolecular combinations of relatively short radicals. Hydrogenation slightly decreases the appearance of these products. Because secondary isoalkanes are often the same as the isoalkanes formed from the branches in polyethylene, their portions in the intensities of the peaks must be known.

The relative intensity $I(n\mathrm{M})$ of the characteristic methylalkane peak was defined as follows:

$$I(n\mathrm{M}) = [A(n\mathrm{M}) \times 1000]/A(\mathrm{C}_i) \quad (3)$$

where $A(n\mathrm{M})$ is the area of the methylalkane peak and $A(\mathrm{C}_i)$ is the area of the next n-alkane peak. In this study, the portion of the secondary reaction products was determined by pyrolyzing a linear HD-polyethylene sample. The true relative methylalkane peak intensities of the branched samples were obtained by reducing the secondary

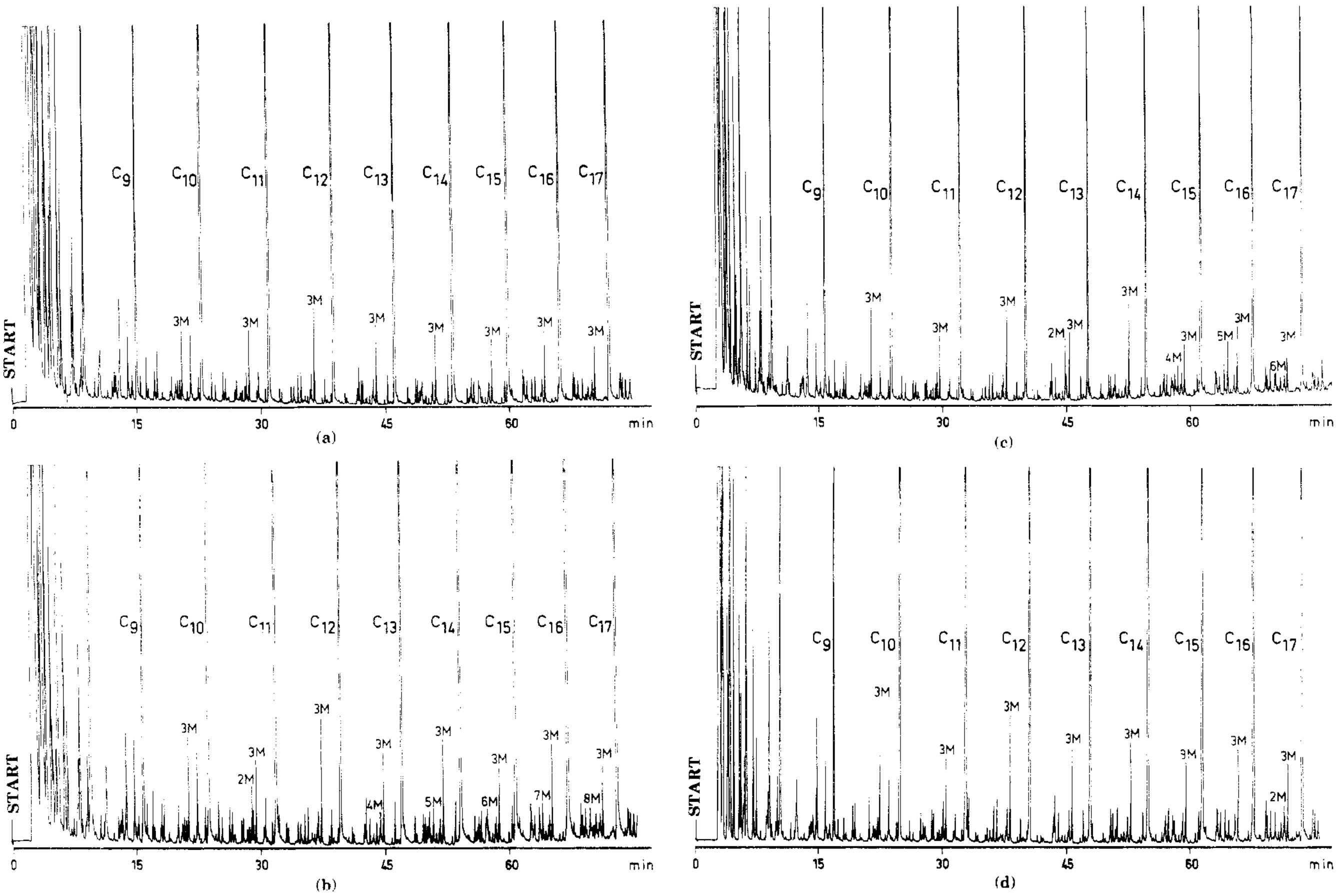


Figure 1. Pyrograms of (a) ethylene–1-butene copolymer, (b) ethylene–1-butene–1-decene terpolymer, (c) ethylene–1-butene–1-dodecene terpolymer, and (d) ethylene–1-butene–1-hexadecene terpolymer.

product portions measured from the pyrogram of the linear HDPE sample.

Sugimura et al.[23] determined correlation factors (f) for methyl, ethyl, and butyl branches, respectively, from the peaks $4MC_{10}$, $3MC_{10}$, and $5MC_{10}$. In general, the f value for different types of branches can be determined as follows:

$$f = \frac{(\text{branch content})/1000\ \text{C} \times 1000}{I(n\text{M})} \tag{4}$$

where $I(n\text{M})$ is the relative intensity of one of the methylalkane peaks formed by β-scission in the polymer backbone. Using eq 3, one may calculate each branch content of the same type of copolymer from the relative peak intensity of the key peak after the secondary product portion has been reduced.

As stated previously, the characteristic peaks for the ethyl branch are 3-methylalkanes, $2MC_{10}$ for the octyl branch, $2MC_{12}$ for the decyl branch, and $2MC_{16}$ for the tetradecyl branch. These peaks can be used for the determination of branch contents in the terpolymers in Figure 1b–d, using ethylene–1-butene, ethylene–1-decene, ethylene–1-dodecene, and ethylene–1-hexadecene copolymers as model polymers. Owing to cleavages in the side chain, ethyl branches have some effect on the formation of 2-methylalkanes, and these longer branches, in turn, affect the formation of 3-methylalkanes in the regions C_{11}, C_{13}, and C_{17}. For this reason, the mutual contribution of the peaks must be taken into account. Table I summarizes the relative intensity of peaks 2M and 3M in the regions C_{11}, C_{13}, and C_{17} and calculated correlation factors for model polymers. After the observed relative intensities of the peaks 2M and 3M in the pyrograms of the terpolymers have been measured, the effective intensity (I_{eff}) can be calculated for each peak. According to Table I, the I_{eff} values for peaks $2MC_{10}$ and $3MC_{10}$ from the pyrogram of ethylene–1-butene–1-decene terpolymer were determined by using eq 5:

Table I
Relative Intensity of Peaks 2M and 3M in the Regions C_{11}, C_{13}, and C_{17}, and Calculated Correlation Factors for Model Polymers

region	copolymer	CH_3/1000 C (IR)	$I(2M)^a$	$I(3M)^a$	f
C_{11}	ethylene–1-butene	16.3	5.5 (0.15)	35.7 (1.00)	457
	ethylene–1-decene	3.3	14.1 (1.00)	2.5 (0.18)	234
C_{13}	ethylene–1-butene	16.3	4.2 (0.08)	51.4 (1.00)	317
	ethylene–1-dodecene	3.8	11.9 (1.00)	1.9 (0.16)	319
C_{17}	ethylene–1-butene	16.3	4.0 (0.08)	47.1 (1.00)	346
	ethylene–1-hexadecene	4.2	10.7 (1.00)	0.5 (0.05)	393

[a] After the secondary product portion has been reduced. Values in parentheses are values relative to the underlined peaks.

$$I(2M)_{\text{eff}} + 0.15I(3M)_{\text{eff}} = I(2M)_{\text{obsd}} \tag{5a}$$

$$0.18I(2M)_{\text{eff}} + I(3M)_{\text{eff}} = I(3M)_{\text{obsd}} \tag{5b}$$

After the $I(2M)_{\text{eff}}$ and $I(3M)_{\text{eff}}$ had been determined the branch content for ethyl (C_E) and octyl (C_O) were obtained by using the correlation factors listed in Table I as follows:

$$C_E = (I(3M)_{\text{eff}}/1000) \times 457 \tag{6a}$$

$$C_O = (I(2M)_{\text{eff}}/1000) \times 234 \tag{6b}$$

Table II
Estimated Branch Contents in Terpolymers

terpolymer	CH_3/1000 C (IR)	I(2M)[a]	I(3M)[a]	branch content/1000 C (PHGC) ethyl	long chain	total	branch content/1000 C (NMR) ethyl	long chain	total
ethylene–1-butene–1-decene	17	19.1[b]	28.3[b]	12	4	16	8	2	10
ethylene–1-butene–1-dodecene	29	48.7[c]	48.7[c]	13	15	28	20	8	28
ethylene–1-butene–1-hexadecene	27	25.3[d]	54.3[d]	18	8	26	20	8	28

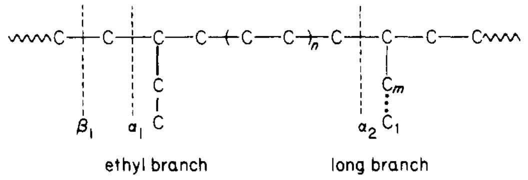
[a] After the secondary product portion has been reduced. [b] Measured from the region C_{11}. [c] Measured from the region C_{13}. [d] Measured from the region C_{17}.

Branch content for the ethylene–1-butene–1-dodecene and ethylene–1-butene–1-hexadecene terpolymers were calculated in a similar manner. Table II summarizes the observed relative intensities of peaks 2M and 3M and the calculated branch contents for the three terpolymers.

According to Table II, the estimated total branch contents in terpolymers obtained by the PHGC method are in reasonable agreement with those obtained by IR and ^{13}C NMR spectroscopy. However, the portions of ethyl and longer branches obtained by PHGC differ to some extent from those obtained from ^{13}C NMR results, especially for ethylene–1-butene–1-dodecene terpolymer. With PHGC, the portion of decyl branches would be 53% of the total branch content, whereas by ^{13}C NMR it would be only 29%.

The total methyl contents in samples and model copolymers were estimated by IR spectroscopy using five standard LDPE samples with average side-chain lengths of four carbons. According to Baker et al.,[26] the extinction coefficient varies with chain length. Compared to a butyl branch, the coefficient will be about 20% higher for the ethyl branch and about 20% lower for the tetradecyl branch. This can cause an error of ±20% in the IR results. The PHGC data were estimated to be reproducible to ±5%. By adding the estimated error in the IR values, the accuracy of the PHGC results was estimated to be ±25%. The accuracy in ^{13}C NMR spectroscopy was estimated to be ±20%. The differences in branch contents between PHGC and ^{13}C NMR determinations were largely due to the inaccuracy in measurements.

Because of the manufacturing procedure, it may be assumed that the branches in model copolymers are randomly situated along the polymer chain. Calculations are based on this assumption. However, in comparing the 3-methylalkane peaks of the terpolymers with those of the ethylene–1-butene model copolymer, one can note a conspicuous difference. The intensities of the peaks $3MC_9$, $3MC_{11}$, $3MC_{13}$, and $3MC_{15}$ in the terpolymers are higher than would be expected from random scissions of the chain. Perhaps 1-butene and long α-olefin have chemically joined the polyethylene chain as follows:



(7)

n = 0, 1, 2, 3, ... (ethylene units)
m = 8, 10 or 14

If n is small, scission at the α_2-position to the long branch is highly probable. Simultaneous scission at the α_1-position results in the increase of n-alkanes C_5, C_7, C_9, C_{11}, etc., and scission at the β_1-position results in the increase of methylalkanes $3MC_5$, $3MC_7$, $3MC_9$, $3MC_{11}$, etc. We may conclude that ethyl and longer branches occur at least in part near each other along the polymer chain. This is supported by the fact that the reactivity of long α-olefins seemed to be connected with the concentration of 1-butene during polymerization. Thus possible changes in scission probabilities caused by exceptional structure may have had some effect on the PHGC results.

The study demonstrates that linear branches up to at least 14 carbons in length can be identified by PHGC. The empirical approach proposed by Sugimura et al.[23] can also be extended to the determination of longer branches. However, this requires high-resolution pyrograms, reproducible PHGC conditions, and, above all, well-characterized model polymers.

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