

Determination of Short-Chain Branches in Poly(vinyl chloride) and Ethylene-Vinyl Chloride Copolymers by Pyrolysis-Hydrogenation-Gas Chromatography

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ABSTRACT: Short-chain branches (SCB) of poly(vinyl chloride) (PVC) and ethylene-vinyl chloride copolymer (EVC) samples were determined by reduction of the samples with tri-*n*-butyltin hydride (Bu₃SnH) followed by high-resolution pyrolysis-hydrogenation-gas chromatographic measurement in the presence of nickel (Ni) as a hydrogenation catalyst. The branch contents were estimated from the relative peak intensities of characteristic key isoalkanes on the C₁₀ and C₁₁ fragment region in the observed pyrograms by comparing the data of reference model ethylene- α -olefin copolymers with known contents of methyl (C₁), ethyl (C₂), and butyl (C₄) branches, respectively. The results obtained by this method were in reasonably good agreement with those found by ¹³C NMR. The correlations between polymerization conditions and the SCB contents in the PVC and EVC samples were also discussed. Significant features of the proposed method such as extremely high sensitivity using less than 1 mg of the sample and rapidness to finish one run in about 1 h would meet the potential needs for the SCB characterization in various polymers containing chlorine, which were used in practical fields.

KEY WORDS Poly(vinyl chloride) / Ethylene-Vinyl Chloride Copolymers / Short-Chain Branches / Pyrolysis-Hydrogenation-Gas Chromatography /

Poly(vinyl chloride) (PVC) and ethylene-vinyl chloride copolymers (EVC) have been among the most widely used polymers because of their excellent cost/performance despite their possible environmental hazard. It has been recognized that morphology and many physical properties of PVC and EVC are dependent upon the kind and the amount of short-chain branches (SCB) along the polymer backbone. Although in early days, IR and γ -radiolysis had been used to study branch structures in PVC, those methods often liable to give disagreeing values of the kind and the amount of branching. Owing to the drastic advances in superconductivity NMR, the SCB numbers of PVC and EVC have been most extensively studied by ¹³C NMR.¹⁻⁷ However, because of stereochemical complications and lack of chemical-shift reference data, it was often difficult to determine the detailed microstructures of PVC and its copolymers directly by ¹³C NMR. Therefore, in most of the studies, PVC and its copolymers were generally reductively dehalogenated into their polyethylene (PE) skeletal structures before spectroscopic characterization because the spectra of the reduced samples can provide significant amounts of information about the structures of the original polymers.

Bovey *et al.*¹ identified the C₁ branch structure (-CH₂C(Cl)H-C(CH₂Cl)H-CH₂C(Cl)H-) in LiAlH₄-reduced PVC by ¹³C NMR. Starnes *et al.*² elucidated the mechanism of the branch formation in PVC by means of ¹³C NMR for LiAlH₄-reduced poly(vinyl- α -*d*-chloride). The same authors³ also demonstrated that the presence of C₄ branch in the PVC might be a result of radical "back-biting" reaction by use of the ¹³C NMR spectra of reductive dehalogenated PVC samples. They also confirmed by the same method that branch

contents were in the order of C₁ > C₄ > C₂ and that no evidence was observed for the existence of C₃ and C₅ branches in PVC.⁵ In our previous papers,⁷ C₁, C₂, and C₄ branches in EVC have been determined by ¹³C NMR for Bu₃SnH-reduced EVC samples.

On the other hand, high-resolution pyrolysis-hydrogenation-gas chromatography (Py-HGC) has been demonstrated to be a valuable technique for studying the branch structures in PE and PVC.^{4,8, 9,10} In these reports, the amounts of SCB were estimated from the relative peak intensities of the characteristic key isoalkanes on the observed pyrograms by use of either platinum (Pt) or palladium (Pd) hydrogenation catalyst where the data for reference model ethylene- α -olefin copolymers with known branch contents were used for calibration.

Ahlstrom *et al.*⁸ determined C₁ and C₂ branches in reductively dehalogenated PVC by Py-HGC using Pd hydrogenation catalyst based on C₇ and C₈ fragment regions on the pyrograms. However, only semi-quantitative results were obtained mainly because of insufficient peak separation. In addition, Liebman *et al.*⁴ also determined C₁, C₂, and C₄ branches in reduced PVC by Py-HGC using the same catalyst and a fused-silica capillary column based on C₁₂ fragment region in the pyrograms combined with a computer simulation technique. This method, however, was limited at most to an inherent detection level of 1 branch/1000 carbon atoms along the polymer chain mostly because of still insufficient resolution of the specific isoalkane peaks on the resulting pyrograms obtained by using the fused silica capillary column at the early days.

In this work, high-resolution Py-HGC was applied to develop a new practical method to determine the amounts of the SCB in PVC and EVC where reductively dehalogenated PVC and EVC samples prepared by

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Table I. Poly(vinyl chloride) samples^a

Sample	Polym. time ^b	Conv. ^c	M_w ($\times 10^{-5}$)	M_w/M_n	Branch contents by ^{13}C NMR ^d		
	h	%			C_1	C_2	C_4
PVC-1	0.5	6.3	0.76	2.0	1.6	0.2	0.3
PVC-2	1	10.2	0.85	2.0	3.0	0.3	0.5
PVC-3	2	22.6	0.91	2.0	5.0	0.5	0.7
PVC-4	3	38.5	0.93	2.1	4.1	0.5	0.8
PVC-5	4	55.1	0.97	2.0	3.1	0.4	0.8
PVC-6	5	70.1	0.98	2.0	3.6	0.7	0.7
PVC-7	6	81.0	1.00	2.0	4.1	0.8	1.1
PVC-8	7	86.7	0.99	2.1	3.7	0.8	1.5
PVC-9	8	93.5	1.00	2.1	4.4	1.1	1.7

^a Polymerization conditions: suspension polymerization initiated by benzoylperoxide in the presence of dispersing agent, polyvinylalcohol by use of an 501 autoclave at 55°C under an initial pressure of 15 kg cm⁻². ^b Polymerization time: 0.5–8 h. ^c Conversion: percent. ^d The SCB number/1000 vinyl chloride monomer units.

Table II. Ethylene-vinyl chloride samples^a

Sample	Ethylene content/mol%			M_w ($\times 10^{-4}$)	M_w/M_n	Branch contents by ^{13}C NMR ^b		
	In feed	In copolymer				C_1	C_2	C_4
		^1H NMR	IR					
EVC-1	2.7	2.0	2.2	13.5	2.6	3.8	0.7	0.7
EVC-2	6.3	5.3	5.9	13.8	2.1	4.3	0.6	1.3
EVC-3	9.0	7.8	9.0	13.9	2.1	4.5	1.1	1.5
EVC-4	17.9	11.1	—	15.3	2.3	4.8	1.0	2.2

^a The polymerization conditions are basically the same as those for PVCs in Table I except for the fed monomers. ^b The SCB number/1000 vinyl chloride monomer units.

using basically the same way reported in the previous papers⁷ was used. Here, various hydrogenation catalysts such as Pt, Pd, and nickel (Ni) were examined for Py-HGC, and various calculation methods were tested for the observed pyrograms to obtain comparable values of the kind and the amount of branches estimated by ^{13}C NMR.

EXPERIMENTAL

Sample

Nine PVC and four EVC samples used in this study are listed in Tables I and II, respectively. The four EVC and their reduced products are the same materials used in the previous work,⁷ and the nine PVC samples were synthesized under basically the same polymerization conditions for the EVCs except for the feeded monomer. The nine PVC samples are also reductively dehalogenated into the PE skeletal structures by using tri-*n*-butyltin hydride (Bu_3SnH) with basically the same procedure reported elsewhere.^{7,11,12} In PVC, the main SCB structures have been reported to be C_1 ($-\text{CH}_2\text{Cl}$), C_2 ($-\text{CH}_2\text{CH}_2\text{Cl}$), and C_4 ($-\text{CH}_2\text{CHClCH}_2\text{CH}_2\text{Cl}$). These SCB structures are thus converted to methyl (C_1), ethyl (C_2), and butyl (C_4) branches in PE skeletal structures by reductive dehalogenation. Furthermore, three model samples, ethylene-propylene (EP), ethylene-1-butene (EB), and ethylene-1-hexene (EH) copolymers, of which branch contents are known to be 20 methyl, 24 ethyl, and 18 butyl per 1000C, respectively, were also used, which are the same materials used in the previous work for SCB determination in PE.¹⁰

Py-HGC Conditions

The Py-HGC system utilized in this work is basically the same as that described previously.^{9,10} A vertical microfurnace-type pyrolyzer (Yanaco GP-1018) was directly attached to a gas chromatograph (HP 5890 SERIES II) equipped with a flame ionization detector (FID) and a fused-silica capillary column (50 m \times 0.2 mm i.d.) coated with immobilized crosslinked methyl silicone gum (0.33 μm film thickness) supplied by Hewlett-Packard (Ultra 1). A weighed sample of ca. 200 μg was pyrolyzed at 650°C under a flow of hydrogen carrier gas (50 ml min⁻¹). The glass insert tube with i.d. of 4 mm in the injection port was packed with hydrogenation catalyst of ca. 2 cm long. In this work, three kinds of hydrogenation catalysts, 5 wt% Pt on 80/100 mesh Diasolid H, 2 wt% Pd on 80/100 mesh Uniport HP and 5 wt% Ni on 60/80 mesh Diasolid H, were used. In the upper part of the glass insert tube, 5 wt% of OV-101 on 80/100 mesh Diasolid H was also packed ca. 1 cm long to protect the catalyst from waxy and less volatile degradation products. The hydrogenation catalyst and OV-101 packing layer were separated and sandwiched by small quartz wool plug. The injection port was maintained at the optimum hydrogenation temperature of 200°C.¹⁰ The hydrogenated products passed through the catalyst tube were introduced into the separation column with a splitting ratio of 50:1. In order to get the optimum separation of the products in C_{10} and C_{11} region on the pyrogram clearly, the separation column temperature was initially set at 40°C, then programmed at a rate of 3°C min⁻¹ to 130°C, and continued to program at a rate of 10°C min⁻¹ up to 300°C. Thus separated components were detected by

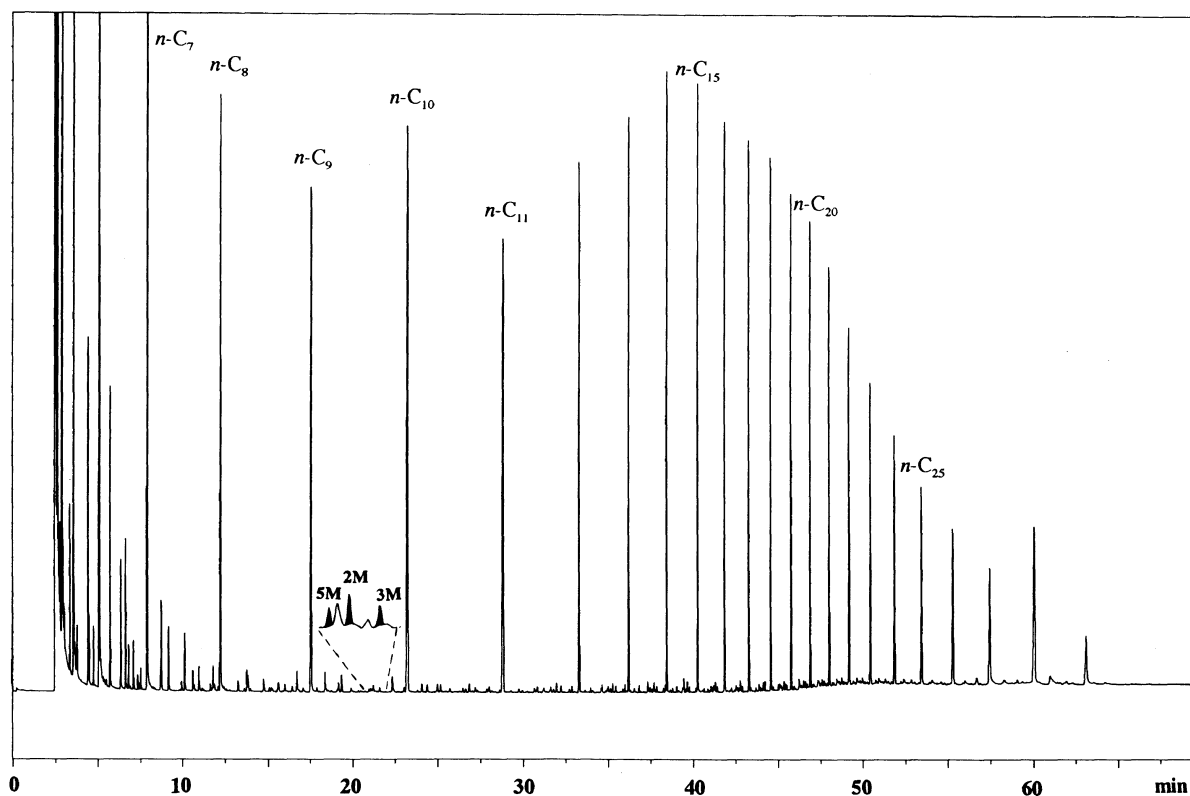


Figure 1. Typical pyrogram of a reductively dehalogenated PVC at 650°C observed after in-line hydrogenation using Ni catalyst. Sample, PVC-6; $n-C_n$, n -alkane with carbon number n ; 2M, 2-methylnonane; 3M, 3-methylnonane; 5M, 5-methylnonane.

Table III. Relative peak intensities of isoalkanes to key peak in the C_{10} region, and observed correlation factor for model ethylene- α -olefin copolymers

Reference sample	Branch content per 1000C	$I(\text{key})_{\text{obs}}^a$	f^b	Relative peak intensities of isoalkanes to key peak ^c		
				2M	3M	5M
P(ethylene- <i>co</i> -propylene)	20C ₁	51.5(2M)	388	<u>1.00</u>	0.093	0.097
P(ethylene- <i>co</i> -1-butene)	24C ₂	52.9(3M)	453	0.489	<u>1.00</u>	0.052
P(ethylene- <i>co</i> -1-hexene)	18C ₄	62.0(5M)	290	0.164	0.080	<u>1.00</u>

^a Key peak intensities relative to peak intensities of $I(n-C_{10})_{\text{obs}} = 1000$. ^b Calculated correlation factor defined by eq 1. ^c The underlined values are those for the key peaks.

FID. The peak identification was mostly carried out by using a gas chromatograph-mass spectrometer (JEOL Automass system II) to which the same pyrolyzer, the hydrogenation catalyst, and the separation column were also attached by using hydrogen carrier gas.

RESULTS AND DISCUSSION

Figure 1 shows a typical pyrogram of reductively dehalogenated PVC (PVC-6) at 650°C where Ni catalyst is used for the in-line hydrogenation. The pyrogram mainly consisting of serial n -alkane peaks is basically the same as that of PE.^{9,10} Various minor peaks, such as 2M, 3M, and 5M in the C_{10} region, observed in-between the main n -alkane peaks are isoalkanes which reflect the branch structures in the polymer chain. Each branch content in the reductively dehalogenated PVCs was determined by the peak simulation using well-defined ethylene- α -olefin model copolymers with known amounts of respective branch structure. Here, only C_1 , C_2 , and C_4 branches were assumed to be present in PVC

according to the foregoing ¹³C NMR studies, and 2-methylnonane (2M), 3-methylnonane (3M) and 5-methylnonane (5M) were selected as the key products for C_1 , C_2 , and C_4 branching, respectively, which were the most intense isoalkane peaks in the corresponding model copolymers. The calculation of branch contents was carried out based on the relative peak intensities of the C_{10} -isoalkanes to n -decane ($n-C_{10}$) in the pyrograms. The correlation factors (f) for the content of branches were calculated first from the corresponding data for the model copolymers with known branch content.

$$\begin{aligned} [I(C_i)_{\text{obs}}/I(n-C_{10})_{\text{obs}}] \times 1000 \times f &= I(\text{key})_{\text{obs}} \times f \\ &= \text{branch number}/1000\text{C} \end{aligned} \quad (1)$$

where $I(C_i)_{\text{obs}}$ is the observed peak intensity of the key isoalkane for C_i branching, and $i = 1, 2$ or 4 . $I(n-C_{10})_{\text{obs}}$ is the observed peak intensity of $n-C_{10}$ alkanes(decane). $I(\text{key})_{\text{obs}}$ is the relative peak intensity of the key isoalkane when the observed peak intensity of $n-C_{10}$ alkanes were regarded as 1000 [$I(n-C_{10})_{\text{obs}} = 1000$].

Table III summarizes the observed $I(\text{key})_{\text{obs}}$ and the calculated f values together with the relative peak intensities of the isoalkanes to the corresponding key peaks for the C_{10} region on the pyrograms of the model copolymers. Because each key peak is not completely independent of others, as pointed out in the previous paper,⁹ the effective peak intensity, I_{eff} for each key peak on the C_{10} region can be calculated by solving the following simultaneous eq 2 when the mutual contributions of the other key peaks observed for the three model copolymers shown in the Table III are considered.

$$\left. \begin{aligned} I(2M)_{\text{eff}} + 0.093I(3M)_{\text{eff}} + 0.097I(5M)_{\text{eff}} &= I(2M)_{\text{obs}} \\ 0.489I(2M)_{\text{eff}} + I(3M)_{\text{eff}} + 0.052I(5M)_{\text{eff}} &= I(3M)_{\text{obs}} \\ 0.164I(2M)_{\text{eff}} + 0.080I(3M)_{\text{eff}} + I(5M)_{\text{eff}} &= I(5M)_{\text{obs}} \end{aligned} \right\} (2)$$

where $I(2M)_{\text{obs}}$, $I(3M)_{\text{obs}}$ and $I(5M)_{\text{obs}}$ are the observed relative peak intensities of the corresponding isoalkanes on the pyrogram of a given reductively dehalogenated PVC regarding the peak intensity of *n*-decane as 1000 [$I(n-C_{10})_{\text{obs}} = 1000$].

Table IV. Observed and effective intensities of key peaks

Sample	Relative intensity of key peaks ^a		
	$I(2M)$	$I(3M)$	$I(5M)$
PVC-1	2.5 (3.4)	0.1 (1.6)	0.6 (1.8)
PVC-2	2.9 (3.9)	0.7 (2.5)	0.6 (1.8)
PVC-3	5.0 (6.5)	0.6 (3.4)	0.6 (2.2)
PVC-4	3.8 (5.1)	1.2 (3.6)	0.7 (2.2)
PVC-5	3.7 (5.0)	0.7 (3.0)	0.7 (2.3)
PVC-6	3.9 (5.3)	0.6 (3.0)	1.0 (2.9)
PVC-7	4.2 (5.7)	0.5 (3.0)	1.0 (2.9)
PVC-8	3.9 (5.3)	1.2 (3.7)	1.4 (3.5)
PVC-9	5.3 (7.3)	1.2 (4.6)	2.0 (5.0)

^a Values relative to $I(n-C_{10})_{\text{obs}} = 1000$. Effective intensities are given first, and observed ones are given in parentheses.

Thus calculated I_{eff} 's for the nine reductively dehalogenated PVCs in C_{10} region are listed in the Table IV along with the observed values, I_{obs} 's. Subsequently, the SCB contents in reductively dehalogenated PVC are calculated by multiplying the I_{eff} by the corresponding correction factor, f , in Table III according to basically the same relation as in eq 1. Additionally, the SCB contents were estimated in a similar manner for the peak intensities in C_{11} fragment region, and for the data obtained using various hydrogenation catalysts for Py-HGC. Thus calculated SCB contents were comparatively summarized in the Table V. Here, the relative peak intensity $I(\text{key})_{\text{obs}}$ observed on the pyrograms was within 1.5% of relative standard deviation (RSD) for three repeated runs, while the estimated branching amounts by use of $I(\text{key})_{\text{obs}}$ and f values estimated from the model copolymers were within 5.5% RSD for three repeated runs.

Among the results shown in Table V, the branch contents calculated by the C_{10} fragment data obtained by use of Ni hydrogenation catalyst proved to be much closer to those estimated by ¹³C NMR. This fact suggests that Ni which is known to be as a less active hydrogenation catalyst than Pt and Pd would be a better catalyst for this purpose. Thus obtained results calculated by the C_{10} fragment data taken by use of Ni catalyst (Table V) exhibit a tendency that C_2 and C_4 contents increase with the increase of the conversion, while C_1 content proved to be almost constant except for the PVC samples at lower conversions up to *ca.* 10%. On the other hand, observed SCB contents obtained by use of Pt or Pd hydrogenation catalyst gave generally fairly big deviations from those by ¹³C NMR, suggesting too strong catalytic actions to trigger undesirable side-reactions during hydrogenation of unsaturated double bond in the pyrolysis products to cause apparently higher branch contents than they were. The observations that

Table V. SCB contents in PVC obtained by Py-HGC using various hydrogenation catalysts and different fragment regions

Fragment region	Sample	Conv. %	Branch contents/1000 chloride monomer units								
			Ni ^a			Pt			Pd		
			C_1	C_2	C_4	C_1	C_2	C_4	C_1	C_2	C_4
C_{10}	PVC-1	6.3	1.8 (1.6)	0.5 (0.2)	0.4 (0.3)	5.5	4.1	2.0	5.3	1.5	1.4
	PVC-2	10.2	2.5 (3.0)	0.5 (0.3)	0.7 (0.5)	5.3	3.8	1.4	5.3	1.0	1.4
	PVC-3	22.6	3.8 (5.0)	0.7 (0.5)	1.0 (0.7)	5.4	3.8	1.8	4.1	1.3	1.9
	PVC-4	38.5	3.2 (4.1)	0.9 (0.5)	1.1 (0.8)	5.1	3.3	1.9	3.8	1.2	0.7
	PVC-5	55.1	3.2 (3.1)	0.9 (0.4)	1.1 (0.8)	5.8	3.5	1.8	4.4	1.6	0.7
	PVC-6	70.1	3.4 (3.6)	1.0 (0.7)	1.1 (0.7)	5.8	3.6	2.1	4.6	1.5	1.0
	PVC-7	81.0	3.6 (4.1)	1.0 (0.8)	1.2 (0.7)	5.6	3.9	2.1	4.5	1.5	1.8
	PVC-8	86.7	3.8 (3.7)	1.1 (0.8)	1.6 (1.5)	5.9	3.7	2.1	4.6	1.4	1.3
	PVC-9	93.5	4.2 (4.4)	1.4 (1.1)	1.7 (1.7)	4.3	4.1	3.0	6.0	1.6	1.8
C_{11}	PVC-1	6.3	3.2	1.7	0.3	5.9	3.9	3.5	6.4	0.1	0.5
	PVC-2	10.2	2.5	1.7	0.3	6.2	2.4	2.8	5.8	1.0	0.5
	PVC-3	22.6	2.5	1.3	0.6	5.9	3.1	3.8	5.6	0.9	0.4
	PVC-4	38.5	2.9	1.3	0.5	5.5	4.4	3.4	6.3	0.6	0.2
	PVC-5	55.1	2.9	1.4	0.6	5.7	3.6	4.8	6.7	0.2	0.2
	PVC-6	70.1	3.4	2.1	0.7	6.3	4.1	3.6	5.5	1.2	0.9
	PVC-7	81.0	3.4	1.7	0.6	6.1	3.4	4.1	5.6	0.7	0.9
	PVC-8	86.7	3.8	2.1	0.8	6.3	3.5	4.0	6.2	1.1	1.5
	PVC-9	93.5	4.6	2.6	0.7	5.9	4.3	3.8	5.8	1.1	1.0

^a The SCB contents determined by ¹³C NMR are given in parentheses.

Table VI. SCB contents in EVC determined by Py-HGC and ^{13}C NMR

Sample	Branch contents/1000 vinyl chloride monomers ^a		
	C ₁	C ₂	C ₄
EVC-1	3.3 (3.8)	0.6 (0.7)	0.5 (0.7)
EVC-2	4.2 (4.3)	1.0 (0.6)	1.3 (1.3)
EVC-3	4.6 (4.5)	1.2 (1.1)	1.6 (1.5)
EVC-4	5.2 (4.8)	1.9 (1.0)	2.2 (2.2)

^a The SCB contents by Py-HGC are obtained based on the C₁₀ region using Ni catalyst, and those obtained by ^{13}C NMR are given in parentheses.

some additional new peaks were detected in the isoalkane regions of the pyrogram taken by use of Pt catalyst, and that relative yields of low-boiling point products eluted before 5 min in the pyrogram for Pd catalyst were approximately twice as much as those for the other catalysts also implicitly support the contribution of the side-reactions in the presence of Pt or Pd other than simple hydrogenation. On the other hand, the observed results based on the C₁₁ region were not completely consistent with those by NMR even for Ni catalyst. These discrepancies might be caused by some overlapping of additional products on the key isoalkane peaks in the C₁₁ region on the pyrograms of the dehalogenated PVCs. This could be improved by using the other separation column with higher resolution.

Then, the same Py-HGC technique by use of Ni catalyst was applied to estimate the SCB contents in the EVC samples listed in Table II. Thus estimated branch contents for the reductively dehalogenated EVC samples are summarized in Table VI. The observed contents which were also in reasonably good agreement with those estimated by ^{13}C NMR shown in the parentheses clearly exhibit a tendency that the SCB contents slightly increase as a monotonously increasing function of ethylene contents in the EVC.

In the former study of low density PEs,¹⁰ the C₁₁ region was empirically selected to estimate the amounts of five kinds of the SCBs (C₁, C₂, C₄, C₅, and C₆) using five different key isoalkane peaks, where the observed amounts of the shorter branches (C₁ and C₄)

had been pointed out to be overestimated than they were, probably because of still remaining some peak overlapping to the corresponding key peaks. In this study for PVCs and EVCs, however, only three isoalkane peaks were focused to be isolated among so many isomers, and therefore both the C₁₀ and C₁₁ region were carefully compared. As might be expected, much more deviation in the observed branching values for C₁ and C₄ were observed for the C₁₁ region, while those by the C₁₀ region gave, in turn, much better results because of the better resolution as for the particular three isoalkane peaks (2-methyl, 3-methyl, and 5-methyl nonane). The C₁₀ region, however, did not still provide better results for the estimation of the SCBs in low density PEs because the whole resolution for the five key isoalkane peaks corresponding to C₁, C₂, C₄, C₅, and C₆ branches in the C₁₀ region proved to be poorer than that in the C₁₁ one.

Since the developed method requires less than 1 mg of the sample and provides a rapid and reproducible measurement within 1 h or so, it would have versatile applicability in the practical field of the SCB characterization for various polymers containing chlorine.

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