EXHIBIT V

PART 20

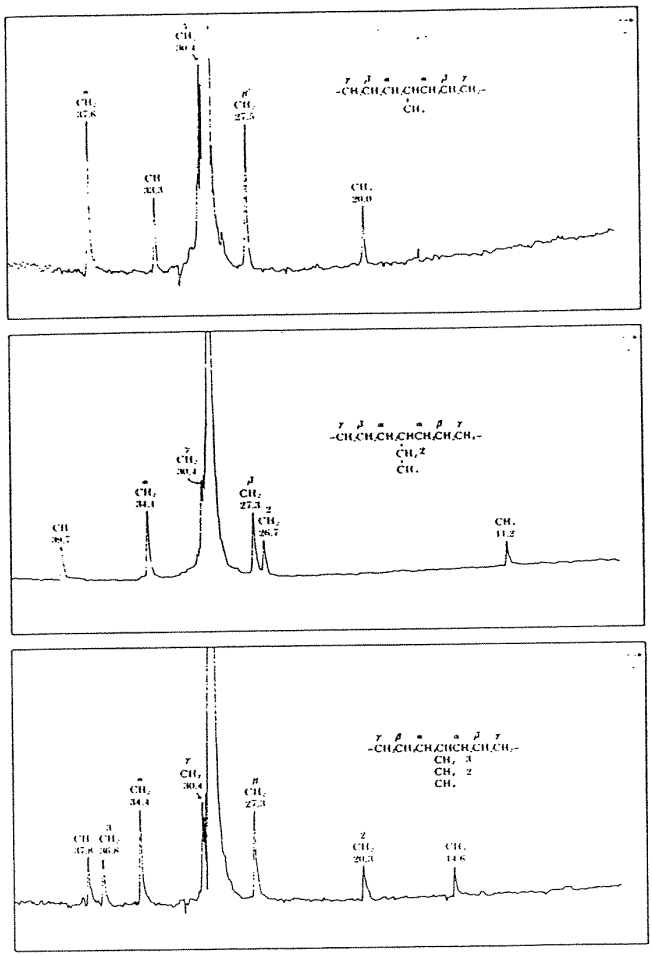

Figure 2. C-13 NMR spectra at 25.2 MHz of (top) *an ethylene-1-propene copolymer,* (middle) *an ethylene-1-butene copolymer, and* (bottom) *an ethylene-1-pentene copolymer*



Figure 3. polymer,

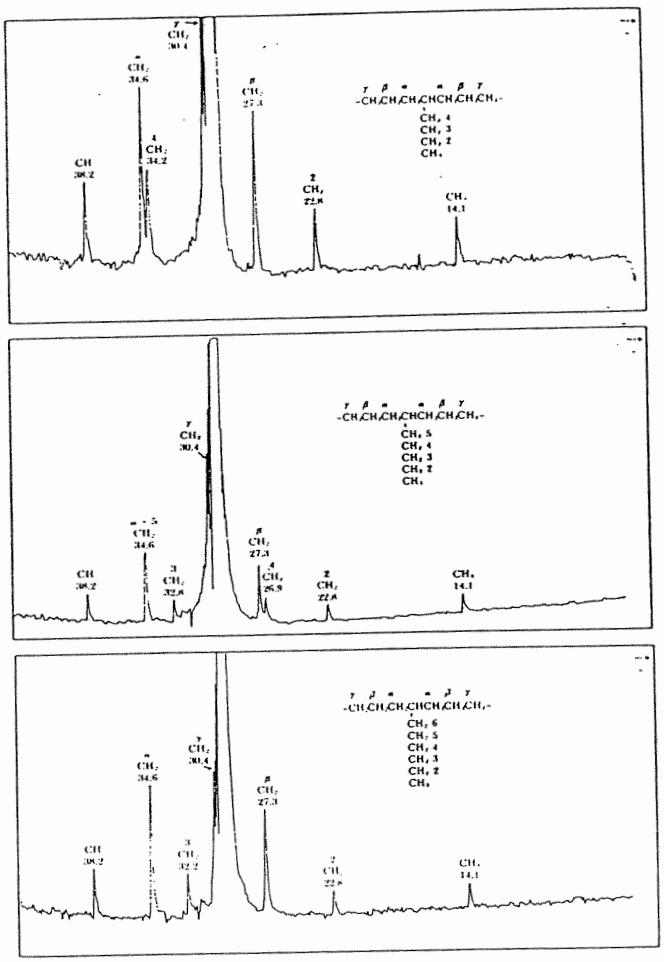

Figure 3. C-13 NMR spectra at 25.2 MHz of (top) *an ethylene-1-hexene copolymer,* (middle) *an ethylene-1-heptene copolymer, and* (bottom) *an ethylene-1-octene copolymer*

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TABLE I

Polyethylene Backbone and Side-Chain C-13 Chemical Shifts in ppm from TMS (±0.1) as a Function of Branch Length (γ Carbon Chemical Shifts, which occur near 30.4 ppm, are not given because they are often obscured by the major 30 ppm resonance for the "n" equivalent, recurring methylene carbons). Solvent: 1,2,4-trichlorobenzene. Temperature: 125°C.

Branch Length	Methine	α	β	1	2	3	4	5	6
1	33.3	37.6	27.5	20.0					
2	39.7	34.1	27.3	11.2	26.7				
3	37.8	34.4	27.3	14.6	20.3	36.8			
4	38.2	34.6	27.3	14.1	23.4	-----	34.2		
5	38.2	34.6	27.3	14.1	22.8	32.8	26.9	34.6	
6	38.2	34.6	27.3	14.1	22.8	32.2	30.4	27.3	34.6

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The capability for discerning the length of short chain branches has made C-13 NMR a powerful tool for characterizing low density polyethylenes produced from free radical, high pressure processes. The C-13 NMR spectrum of such a polyethylene is shown in Figure 4. It is evident that the major short chain branches are butyl, amyl and ethyl. Others are also present, and Axelson, Mandelkern, and Levy, in a comprehensive study (6) have concluded that no unique structure can be used to characterize low density polyethylenes. They have found nonlinear short chain branches as well as 1,3 paired ethyl branches. Bovey, Schilling, McCracken and Wagner (9) compared the content of branches six and longer in low density polyethylenes with the long chain branching results obtained through a combination of gel permeation chromatography and intrinsic viscosity. An observed good agreement led to the conclusion that the principal short chain branches contained fewer than six carbons and the six and longer branching content could be related entirely to long chain branching. Others have now reported similar observations in studies where solution-methods are combined with C-13 NMR (10). However, as a result of the possible uncertainty of the branch lengths, associated with the resonances for branches six carbons and longer, C-13 NMR should be used in conjunction with independent methods to establish true long chain branching.

From the results we have seen thus far, it is easy to predict the C-13 NMR spectrum anticipated for essentially linear polyethylenes containing a small degree of long chain branching. An examination of a C-13 NMR spectrum from a completely linear polyethylene, containing both terminal olefinic and saturated end groups, shows that only five resonances are produced. A major resonance at 30 ppm arises from equivalent, recurring methylene carbons, designated as "n", which are four or more removed from an end group or a branch. Resonances at 14.1, 22.9 and 32.3 ppm are from carbons 1,2 and 3, respectively, from the saturated, linear end group. A final resonance which is observed at 33.9 ppm, arises from an allylic carbon, designated as "a", from a terminal olefinic end group. These resonances, depicted structurally below, are fundamental to the spectra of all polyethylenes.

$$\underset{\quad 1 \quad 2 \quad 3}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}} \qquad \underset{\text{"n"}}{\text{-}(CH_2)_n\text{-}} \qquad \underset{\text{"a"}}{\text{-}CH_2\text{-}CH{=}CH_2}$$

An introduction of branching, either long or short, will create additional resonances to those described above. For long chain branches, these will be an α, β, (and sometimes γ) and a methine resonance as depicted structurally below:

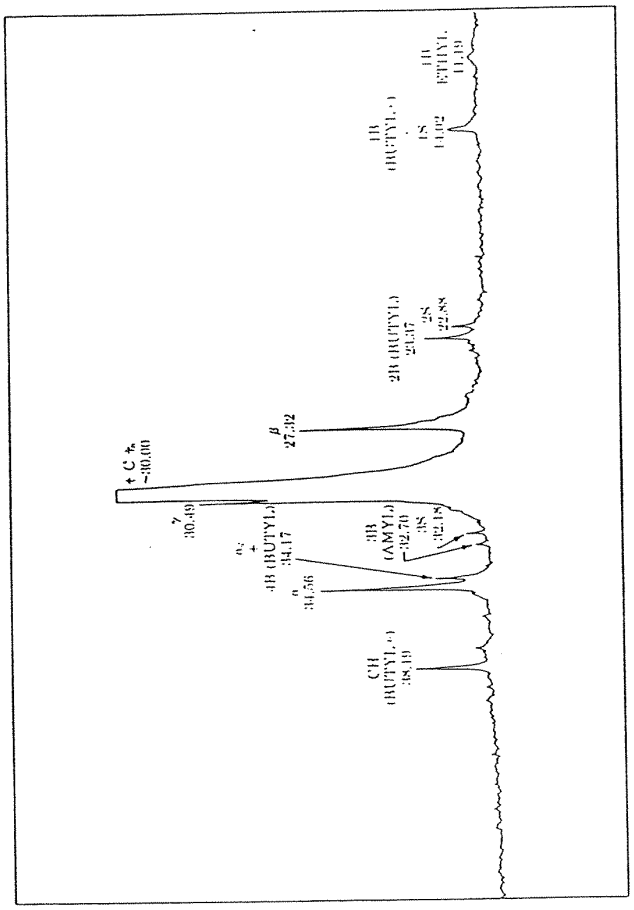

Figure 4. C-13 NMR spectrum at 25.2 MHz of a low-density PE produced from a high-pressure process

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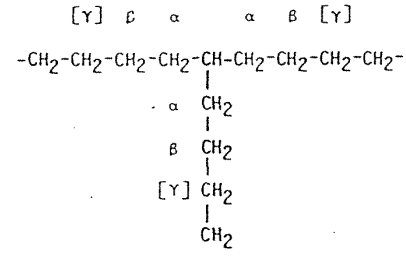

From the observed C-13 NMR spectrum of the ethylene-1-octene copolymer (Figure 3), we find that the α, β and methine resonances associated with branches six carbons and longer occur at 34.56, 27.32 and 38.17 ppm, respectively. Thus in high density polyethylenes, where long chain branching is essentially the only type present, carbon-13 NMR can be used to establish unequivocally the presence of branches six carbons long and longer. If no comonomer has been used during polymerization, it is very likely that the presence of such resonances will be indicative of true long chain branching. In any event, C-13 NMR can be used to pinpoint the absence of long chain branching and place an upper limit upon the long chain branch concentration whenever branches six carbons and longer are detected.

The need for a complementary measurement to C-13 NMR in studies of long chain branching should be apparent. It has been pointed out that a promising possibility appears to be flow activation energies obtained from dynamic shear moduli as a function of temperature (20). Flow activation energies range from approximately 6.0 kcal/mol for linear systems to around 13.5 kcal/mol for systems containing extensive long chain branching. Chain entanglements are one of the factors influencing flow activation energies, but to the extent that long chain branches also influence chain entanglements, this technique can be an indicator of the presence of long chain branching. Four polyethylenes, labelled "A" through "D" and selected for C-13 NMR characterization on a basis of the observed flow activation energies, are described in Table II. A fifth polymer, called "E", was also examined as a reference polymer because it was not expected to contain any significant long chain branching as indicated by its flow activation energy (see Table II). Carbon-13 NMR data were obtained at a high field (50 MHz, 47 kG) to achieve improved sensitivity. The 50 MHz spectra of these polymers, A through E, are reproduced in Figures 5 through 9. Instrumental conditions necessary for quantitative measurements will be discussed later; for the present, we will be concerned with the use of C-13 NMR as a means for simply detecting the presence of long chain branching.

Figure 4. C-13 NMR spectrum at 25.2 MHz of a low-density PE produced from a high-pressure process

TABLE II

Molecular Weights, Flow Activation Energies and Type of Catalyst for a Series of Polyethylenes Examined for Long Chain Branching.

Polymer	M_w	M_n	E_a	Catalyst	Comonomer	"g" factor*
A	159,000	19,100	8.0 kcal/mol	chromium based	None	0.8
B	224,000	13,600	8.6 kcal/mol	chromium based	None	0.5
C	148,000	17,900	9.3 kcal/mol	chromium based	None	0.6
D	226,000	8,500	9.6 kcal/mol	chromium based	Hexene-1	0.7
E	172,000	32,400	6.1 kcal/mol	titanium based	None	(1+)

*These "g" factors are probably not very accurate. See text.

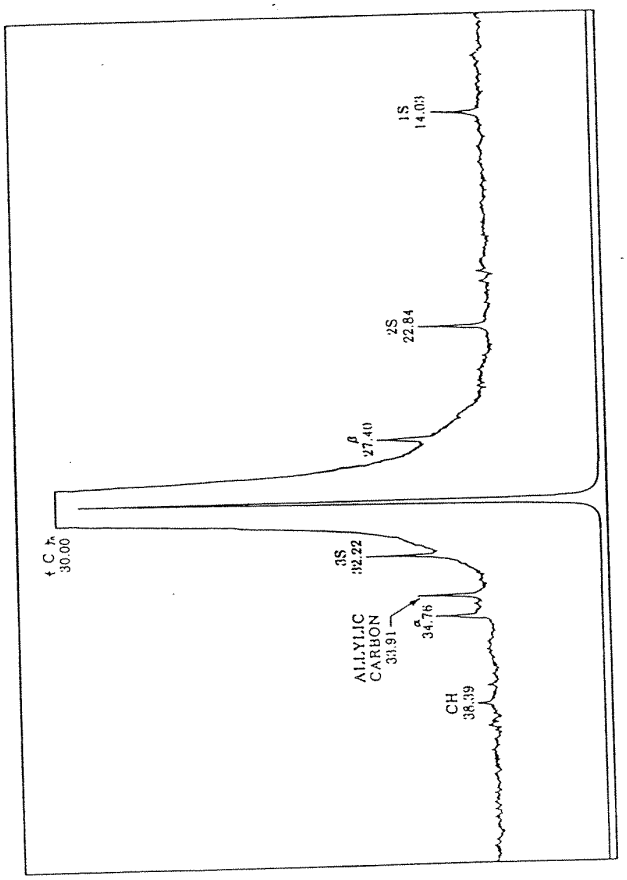

Figure 5. C-13 NMR spectrum at 50 MHz of Polymer A (~ 75% in trichlorobenzene at 125°C, number of transients accumulated 45,300). Spectrum was provided courtesy of Nicolet Technology Corporation.

*These "g" factors are probably ... [illegible]

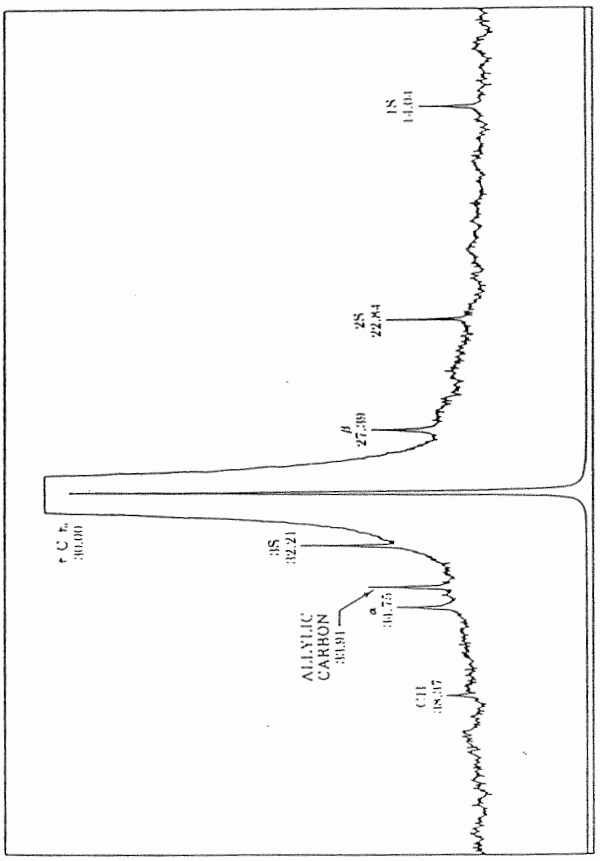

Figure 6. C-13 NMR spectrum at 50 MHz of Polymer B (~ 75% in trichlorobenzene at 125°C, number of transients accumulated 4,900). Spectrum was provided courtesy of Nicolet Technology Corporation.

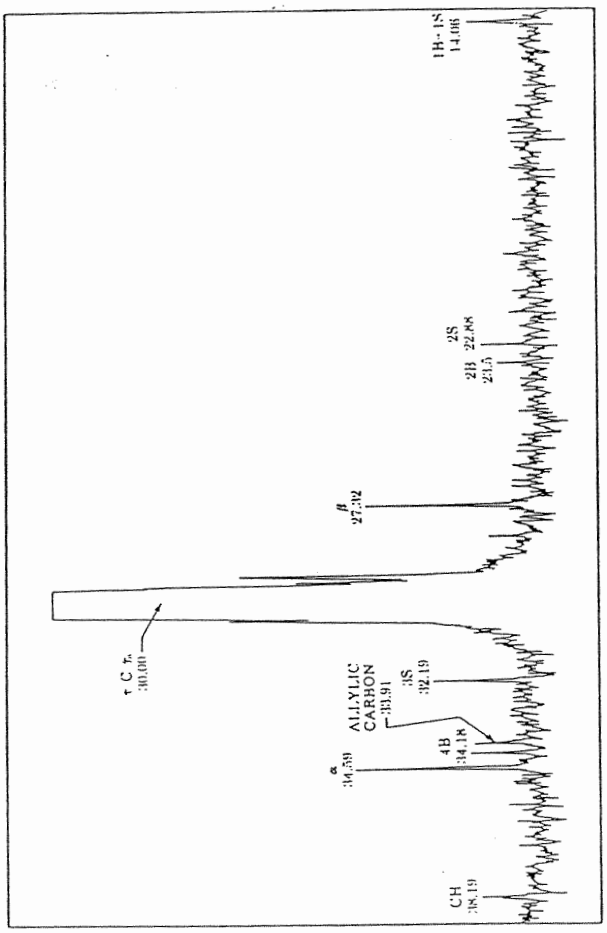

Figure 6. C-13 NMR spectrum at 50 MHz of Polymer B (~ 75% in trichlorobenzene at 125°C, number of transients accumulated 4,900). Spectrum was provided courtesy of Nicolet Technology Corporation.

Figure 7. C-13 NMR spectrum at 50 MHz of Polymer C PE homopolymer (~ 10% in trichlorobenzene at 125°C, number of transients accumulated 50,000). Spectrum was provided courtesy of Varian Associates.

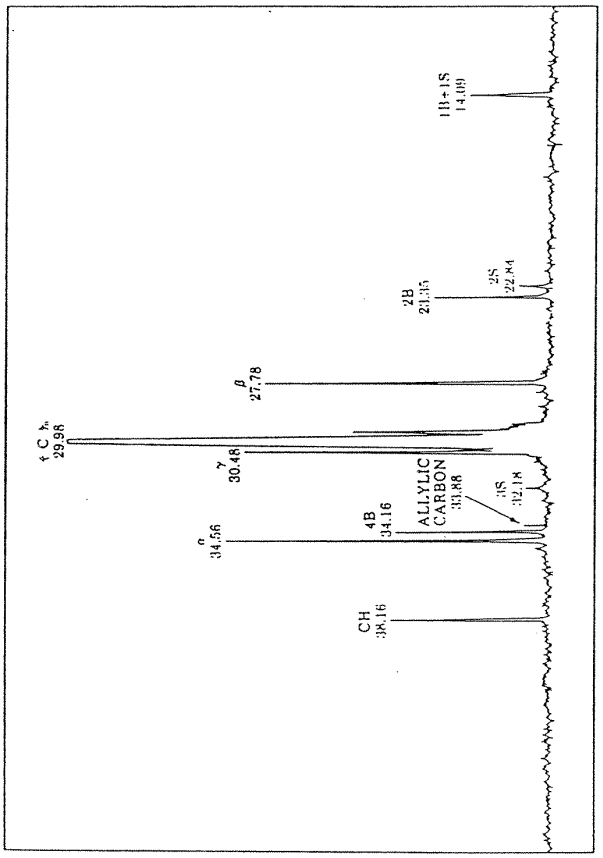

Figure 8. C-13 NMR spectrum at 50 MHz of Polymer D ethylene-1-hexene copolymer (~ 10% in trichlorobenzene at 125°C, number of transients accumulated 8,743). Spectrum was provided courtesy of Varian Associates.

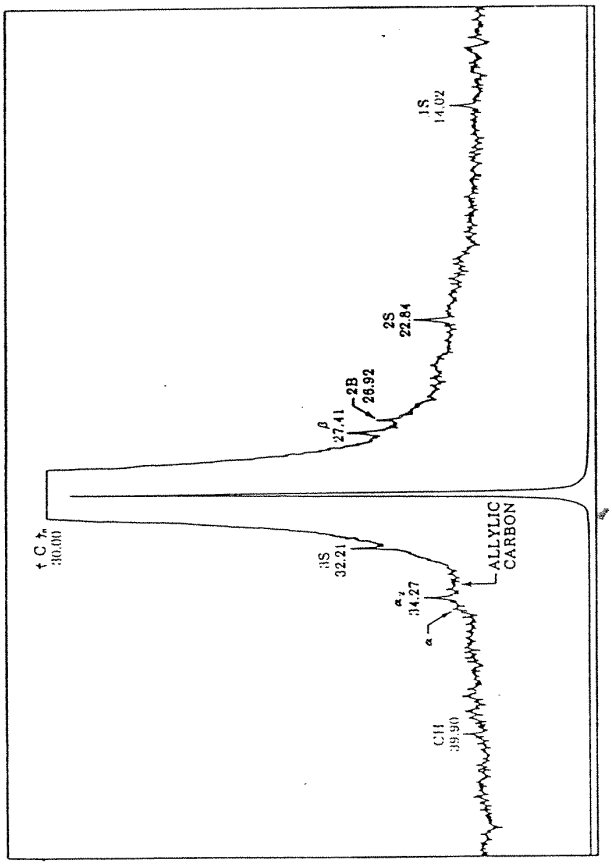

Figure 8. C-13 NMR spectrum at 50 MHz of Polymer D ethylene-1-hexene copolymer (~ 10% in trichlorobenzene at 125°C, number of transients accumulated 8,743). Spectrum was provided courtesy of Varian Associates.

Figure 9. C-13 NMR spectrum at 50 MHz of Polymer E (~ 75% in trichlorobenzene at 125°C, number of transients accumulated 10,100). Spectrum was provided courtesy of Nicolet Technology Corporation.

For those polyethylenes where short chain branching is present in addition to long chain branching (see Figures 8 and 9), a modification in the nomenclature scheme is needed to distinguish identifiable short chain carbon resonances from the corresponding carbons in chain end groups. Consequently, an "S" (for saturated end groups) has been added to the 1, 2 and 3 carbon nomenclature for chain ends. The numbers for carbons in branches of length five and shorter have a "B" added. In figures 5-9, the resonances from chain ends, six and longer, are clearly identified from carbon resonances from the short side-chain branches.

The 50 MHz C-13 NMR spectrum of polymer "A" is reproduced in Figure 5. It is nearly a classical representation of the spectrum anticipated for a polyethylene containing long chain branching. Only the five resonances expected for linear polyethylene systems plus the α, β, and methine resonances for long chain branches are observed. A simple inspection of the α, β intensities as compared to the end group resonances indicates that fewer than one polymer molecule out of three has a long chain branch. A similar result was obtained for polymer "B" shown in Figure 6. Both polymers "A" and "B" contain long chain branches and, on an average, have approximately equal numbers of both saturated and terminal olefin end groups.

Polymer "C", shown in Figure 7, gives a more complex C-13 NMR spectrum than observed for polymers "A" and "B" because four-carbon side-chain branches are positively indicated even though no comonomer was added during polymerization. The presence of butyl branches complicates an identification of long chain branching because the α, β resonances from butyl branches have the same chemical shifts as do the α, β resonances from longer, linear branches (see Table I). The long chain branching for systems containing butyl branches, therefore, can only be determined from the differences observed in the relative intensities for the "4" carbon and the α carbon. In Figure 3, the α to "4" carbon resonance intensities are distinctly 2:1. In Figure 7, the relative intensities for the α to "4" carbon resonances are 2.7:1 and long chain branching is, therefore, indicated. The polymerization conditions have somehow led to an introduction of butyl branches without also introducing amyl branches or branch lengths shorter than four. This result is interesting and leads to the suggestion that the long chain branches in polymer "C" may not be truly "long". A disproportionate number of these "long chain" branches may be intermediate in length. Further study is clearly indicated for this polyethylene system. Without C-13 NMR, however, one may not have been aware that short chain branches were being introduced into a polyethylene polymerization without adding comonomer.

Polymer "B" is an ethylene-1-hexene copolymer by design. A flow activation energy of 9.6 kcal/mol suggests that long chain branching may be present. The C-13 NMR spectrum, however, is complicated by the presence of butyl branches as in the case of

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polymer "C". Once again, the detection of long chain branching must be based on a ratio of the observed intensities for the "α" carbon resonance to the "4" carbon resonance, which is 2.04 in this case and within experimental error of the NMR intensity measurements. Thus long chain branching cannot be determined readily unless one resorts to a tedious set of measurements designed to establish whether the excess intensity of the "α" resonance is outside the limits of experimental error.

Polymer "E" was prepared with a Ziegler type of catalyst and has only a small quantity of terminal olefin end groups, as shown by the NMR spectrum in Figure 9. It was not expected to have any significant degree of long chain branching because the flow activation energy was 6.1 kcal/mol. The C-13 NMR spectrum is consistent with the presence of very low quantities of long chain branching (see "α" in Figure 9). An unexpected result did occur, however, because ethyl branches could be clearly identified by the chemical shifts for the "α_2", "β", methine and side-chain carbon resonances. Note in Figure 9 that the methyl resonance for the ethyl branch is not shown; the others can be clearly identified in Figure 9).

From a quantitative viewpoint, it is evident that the relative intensities of the resonances from carbons associated with branches and end groups can be compared to the intensity for the major methylene resonance, "n", at 30.00 ppm to determine branch concentrations and number average molecular weight or carbon number. The following definitions are useful in formulating the appropriate algebraic relationships:

n = intensity of the major methylene resonance at 30 ppm

$\bar{s}$ = average intensity for a saturated end group carbon

a = the allylic carbon intensity at 33.9 ppm

C_{tot} = the total carbon intensity

$\bar{\alpha}$ = 1/2 (α + β) carbon intensities

N = average number of long chain branches per polymer molecule

N+2 = average number of end groups per polymer molecule

With the previous definitions, the polymer carbon number and number average molecular weight are given by:

$$\text{Carbon Number} = C_{tot}(N+2)/(\bar{s} + a) \quad (1)$$

$$M_n = 14 \times \text{Carbon Number} \quad (2)$$

For linear polymers where "N" is zero, the carbon number and number average molecular weight can be easily and reliably determined. For those polymers containing long chain branching, one must utilize the ratio of the carbon resonance intensities associated with branching to the end group carbon resonance intensities to determine "N" as follows:

$$N = 2\,\bar{\alpha}/\,(3(\bar{s} + a) - \bar{\alpha}) \quad (3)$$

The number of long chain branches per ten thousand carbon atoms is similarly given by:

$$\text{Branches/10,000 C} = ((1/3\,\bar{\alpha})/(C_{tot} \times 10^4)) \quad (4)$$

Equation 4 can be easily modified for the number of short chain branches (fewer than six carbons) per 10,000 carbons by replacing 1/3 α with an intensity appropriate for one branch carbon from the short chain branch.

With the comprehensive structural information available from C-13 NMR analyses of both low and high density polyethylenes, quantitative measurements become highly desirable. As seen from equations 1-4, the quantitative relationships necessary for analyses of branching, molecular weight and end group distributions can be readily derived without resorting to limiting assumptions. The assignments have been rigorously established; thus the only question remaining is the reliability of the data with respect to the observed relative intensities. Differences among nuclear Overhauser effects, non-equilibrium dynamic conditions during data gathering and software-hardware problems with the dynamic range are factors which would adversely affect the relative observed C-13 NMR spectral intensities.

It has been demonstrated by Levy and coworkers (6)(21) that nuclear Overhauser effects in polyethylenes are full and, therefore, are not a consideration under the experimental conditions (~10% solutions, 125°C) employed in C-13 NMR quantitative measurements of polyethylene. Because the C-13 NMR experiment utilizes the Fourier transform technique and free induction decay data is gathered in a time dependent framework, spin-lattice relaxation times, T_1's, are important factors that must be considered when designing a pulse sequence for long term data averaging. Generally, the pulse spacings must be five times the longest observed T_1 to ensure complete relaxation between rf pulses (22). The methyl groups in chain ends and short branches can have T_1's ranging from 3 to 7 seconds (21); thus the time re-

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quired to gather three to five thousand FID's can become inordinately long. When planning quantitative experiments on well-known systems, it is advisable to select those resonances most favorable from a T_1 standpoint for quantitative measurements because instrument time is expensive and should be used efficiently.

Dynamic range is an important consideration in quantitative NMR measurements because small resonances may become truncated with respect to large resonances (≥1000:1) during time averaging if a sufficient computer word length is not available (23). It is imperative in measurements of long chain branching in polyethylene that an NMR instrument be equipped with either a 16K computer system with block averaging or have a 16K computer system with either double precision or floating point arithmetic. Instruments are now available that have both double precision and floating point arithmetic, which are also valuable in preventing unwanted truncations during Fourier transformations. With reasonable care given to both the software and hardware problems associated with quantitative C-13 NMR of polymers, one finds that measurements of end group distributions, molecular weight, and branching in polethylene are routinely available.

One of the best tests for satisfactory NMR instrumental conditions during quantitative C-13 NMR measurements is to examine known reference standards. The best for this purpose are NBS standards 1482 (M_w = 13,600, M_n = 11,400) and 1483 (M_w = 32,100, M_n = 28,900). The NBS standard 1483 was examined under precisely the same experimental NMR conditions as polyethylenes C and E reported in Table II. The C-13 NMR spectrum is shown in Figure 10. Instrumental conditions and pertinent intensity data are given below:

	Resonance	Peak Height	Assignment
Pulse Angle: 50°	32.18 ppm	4.5	3S
Pulse Spacing: 1 second	33.91 ppm	1.1	"a"
Double Precision Arithmetic	30.00 ppm	6082	"n"
	34.09 ppm	3.9	α_2

M_n = 30,560 (Calculated from Equations 1 and 2).

(Only 3S was used to determine $\bar{s}$ because it has the shortest T_1 of the three terminal carbons.)

As was the case for polymer "E", a small amount of ethyl branching was detected in NBS 1483 as indicated in Figure 10 by the resonances observed for the appropriate methine, α_2, β and 2B carbons. (The methyl resonance is not shown.) The concentration of ethyl branches is 3 per 10,000 carbons as determined using a modified version of Equation 4. NBS 1483 was probably prepared using a Ziegler type catalyst system, as suggested by the rela-

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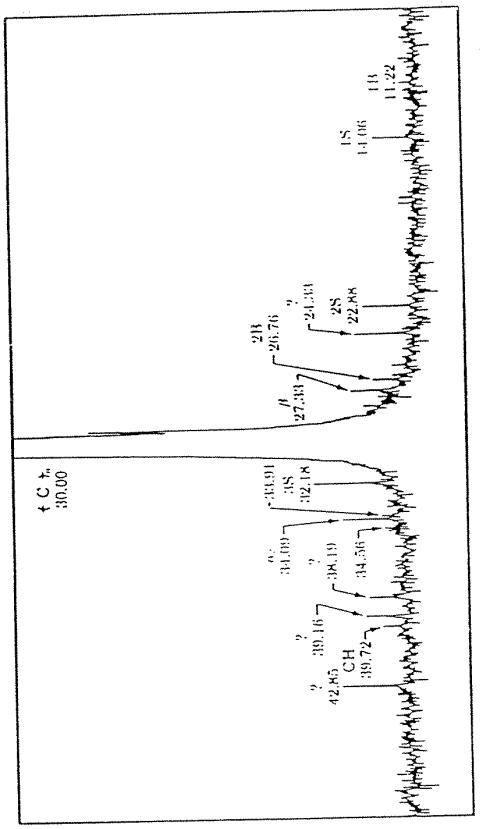

Figure 10. C-13 NMR spectrum at 50 MHz of NBS 1483 (~ 10% in trichlorobenzene at 125°C, number of transients accumulated 229,462). Spectrum was provided courtesy of Varian Associates.

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tively low intensity of the 33.9 resonance for the allylic carbon. It is interesting that a low amount of ethyl branching was detected in this sample and in polymer "E", which was prepared with a Ziegler type catalyst. *NBS 1482 was examined using an XL-100 spectrometer at 25 MHz.* Instrumental conditions and intensity data are given below:

	Resonance	Peak Height	Assignment
Pulse Angle: 90°	14.09 ppm	11	1S
Pulse Spacing: 10 seconds	22.86 ppm	15	2S
Double Precision Arithmetic	32.16 ppm	14	3S
	33.00 ppm	8	"a"
	29.98 ppm	9574	n

$\bar{s}$ = 14.5 (1S was not used).

M_n = 11,970 (Calculated from Equations 1 and 2).

Ethyl branching was not detected in NBS 1482; however, the instrumental sensitivity was such that branching in a range of 1-5 per 10,000 carbons would not be observed. The agreement between the number average molecular weights calculated from the NMR data and that reported by NBS serves to indicate the viability of the NMR method for determining number average molecular weight. The method discussed above, when applied to the C-13 NMR data from polymers A through E, gave the results listed in Table III for M_n, N and degree of branching.

TABLE III

Number Average Molecular Weight, Long Chain Branching, Short Chain Branching and End Group Distribution for Polymers A, B, C, D and E.

Polymer	C_{6+} Branches/ Molecule	Branches/10,000		Mn	s/a
A	0.28	(C_{6+})	1.8	21,700	1/1
B	0.29	(C_{6+})	2.1	18,680	1/1
C	0.23	(C_{6+})	1.4)	23,100	1/7.1
		(Butyl)	5.5)		
D	----	(Butyl)	64	10,300	1/1
E	----	(Ethyl)	2.2	28,650	2.2/1

Number average molecular weight data from size exclusion chromatography for polymers A through E has been given previously

in Table II. These results should be compared to the number average molecular weights obtained from NMR in Table III. In size exclusion chromatography, both linear and branched molecules are separated according to their respective hydrodynamic volumes, that is

$$n_{lin}M_{lin} = n_{br}M_{br}, \quad (5)$$

the principal of universal calibration (18). In this particular SEC analysis, no consideration was given to the possibility that the polymer molecules could be branched; thus low molecular weight results should be anticipated because branched polymers have overall smaller dimensions than linear polymers of the same molecular weight. Lower results were obtained as shown by the data in Table II although the internal trends are identical to those obtained from NMR. It is possible to use the number average molecular weights from SEC and NMR to calculate the familiar "g" factor (18) through the relationship,

$$g^{1/2} = n_{br}/n_{lin} \quad (6)$$

and equation 5. Values of "g" less than one were obtained although they are somewhat smaller than the values predicted by Zimm and Stockmayer (24) for the amount of long chain branching determined by NMR. The differences could be easily accounted by the error (± 10% in the molecular weights from SEC). Although these "g" factors are probably inaccurate, they are in the correct direction from the NMR data and from SEC.

Polymer "E" gave the highest number average molecular weight of the polymers examined, and for this reason, it probably gave the least accurate result from both NMR and SEC, which are probably within experimental error. The error in the NMR measurement will increase with molecular weight unless an effort is made to obtain spectra with the same signal-to-noise ratio for the respective resonances associated with branches. The utility and accuracy of the C-13 NMR method in providing quantitative polymer structural data, however, is gratifying.

The C-13 NMR method has been criticized in the past because it is time consuming. Five to ten thousand transients with 10-15 seconds pulse delays are usually required with 10-15% by weight solutions to obtain signal-to-noise adequate for a one part in one thousand measurement. This time factor can be reduced substantially if one uses twenty millimeter sample tubes and a superconducting magnet system and examines the polyethylene in a melt state. This improvement plus the fact that three measurements, number average molecular weight, end group distribution and degree of branching, are accomplished in one make C-13 NMR a highly attractive method for characterizing polyethylenes. A

serious drawback is not encountered even though branches six carbons in length and longer are measured collectively. The short branches are generally less than six carbons in length and truly long chain branches tend to predominate. On occasions, there may be special exceptions for "intermediate" branch lengths, as shown by polymer "C" in this study, so independent rheological measurements should be sought as a matter of course. Nevertheless, a direct method, which possesses the required sensitivity to determine long chain branching in high density polyethylenes, is now available.

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THE ROLE OF COMONOMER TYPE AND DISTRIBUTION IN LLDPE PRODUCT PERFORMANCE

BY

L.D. CADY

THE DOW CHEMICAL COMPANY

INTRODUCTION

Polyethylene physical properties are primarily determined by the degree of crystallinity and the molecular weight of the polymer. The degree of crystallinity is affected by the type, number, and distribution of branches along the polymer chain. During film fabrication, molecular weight and molecular weight distribution play an important role in final resin properties in that crystallization rate and melt flow properties are strongly influenced by these parameters.

Linear Low Density Polyethylene (LLDPE) is manufactured by copolymerizing ethylene with a selected α-olefin. It is characterized as having only short chain branches in contrast to the presence of both short and long chain branching in high pressure LDPE.

The type, number, and distribution of branches in LLDPE are determined by comonomer, catalyst and process. The length of the branch is strictly a function of comonomer length. For example, octene-1 yields hexyl branches, while copolymerization with butene-1 yields ethyl branches. The number of branches in LLDPE is controlled by the amount of comonomer incorporated, which in turn determines the density of the copolymer. The distribution of branches in the copolymer is influenced by comonomer type, but does not exhibit a primary relationship such as that seen with length or number of branches. In contrast, catalyst and process are the primary variables responsible for determining branch distribution.

Short chain branching distribution (SCBD) can be discussed from several perspectives. The two primary components of SCBD are intramolecular distribution (distribution and branches along a single copolymer chain) and intermolecular distribution (the relative ratio of comonomer to ethylene in all of the copolymer chains). Temperature rising elution fractionation (TREF) can lend considerable insight into intermolecular branching distribution, and is the analytical technique discussed in this paper. The application of TREF provides understanding in the relationship of SCBD to film properties, and provides a means of describing an additional fundamental resin parameter to complement molecular weight, molecular weight distribution, and density.

EXPERIMENTAL

Materials and Equipment

The resins used in this study are all solution process ethylene/α-olefin copolymers, and are described in Table I. The resins were chosen such that molecular weight, molecular weight distribution, and density were comparable so that the effect of comonomer length and distribution could be studied independently.

The films were fabricated on a 2 1/2", 24/1 L/D Egan extruder with a 6" Uniflo die and dual lip Uniflo air ring. All physical property testing was performed according to applicable ASTM methods.

Fractionation Techniques

Temperature Rising Elution Fractionation (TREF) was the technique chosen for this work. It is a method of polymer fractionation based on the principle that at a given temperature, the solubility of a semi-crystalline polymer such as polyethylene depends on the crystallinity of that fraction. The method of TREF was first used by Desreux and Spiegels and later by several other groups.[2-7] TREF is especially useful in that fractions can be collected and characterized by melting point, branch content, and molecular weight. Adaptations of TREF which employ continuous polymer mass monitoring are also described in the literature and used in this study.[4,5] The mass distribution

of crystallinity obtained by this modified TREF technique provides a useful "fingerprint" of polyethylene resins without the necessity of isolating POLYMER FRACTIONS.

Polymer Characterization

The whole polymers and fractions of each were characterized in terms of thermal analyses, comonomer content and molecular weight. Melting and freezing curve profiles were determined using a Perkin-Elmer DSC-2C differential scanning calorimeter. Comonomer content was calculated from CH_3/1000C determination according to ASTM D2238-68 using a Beckman 4260 infrared spectrophotometer. Molecular weight and molecular weight distributions were determined using melt flow (I_2) and melt flow ratio (I_{10}/I_2) measurements.

RESULTS AND DISCUSSIONS

The use of the TREF technique allows for workable fractions of the polymer, sufficient in size for determination of melting point, branching, and molecular weight. The relationship between melting point and elution temperature was demonstrated to be linear with increasing elution temperature corresponding to increasing melting point. This relationship is shown in Figure 1, and was found to be independent of branch length.

Wild, et. al., reported a similar relationship which coupled branching content in the fractions with elution temperature. This information was used to construct a calibration curve, which was in turn used for a small scale continuous mass monitoring fractionation. From this, they were able to construct a mass distribution of polymer vs. branch content.[4] This work confirmed that relationship to be linear; however, it was also found that branch length played an important role in the absolute number of branches corresponding to a given elution temperature. Figure 2 shows the different calibration curves for this work constructed for an ethylene/butene copolymer and an ethylene/octene copolymer. While both relationships exhibit linear character, the slope of each is dependent on branch length. From the above, it follows that melting point and branch content is also a linear

relationship, and is dependent on branch length. Figure 3 shows the melting point vs. branch content for the ethylene/butene and ethylene/octene copolymers of this study.

Elston has also reported the relationship between branch content and melting point for ethylene/ α-olefin copolymers.[8] His work showed that the relationship was linear, but variable in that the degree of heterogeneity of the polymer affected its melting point. He showed that homogeneous copolymers exhibit a lower melting point than their more heterogeneous counterparts with equivalent branch content. This phenomenon can be easily studied using TREF. In this study, the fractions and whole polymers were analyzed by DSC and the results compared to theoretical equilibrium melting points calculated from Flory's copolymer melting equilibrium depression equation.[9] Modifications to the Flory equation were made to correct for branch carbons which interfere with infrared measurement of backbone carbons when determining CH_3/1000C atoms. Figure 4 shows the comparison of the melting point equation with whole polymer and fraction melting points of an ethylene/octene and an ethylene/butene copolymer. While the whole polymer melting points deviate substantially from the equation, the corresponding fractions exhibit much better agreement. This indicates that while each fraction is relatively homogeneous, the combinations of the fractions result in a heterogeneous copolymer.

Characterization of polymers as to the above relationship provides information on two phases of copolymer heterogeneity; the first being the deviation of whole polymer melting point from theoretical values, and the other being fraction melting point deviation from the line. At least one source of heterogeneity of the whole polymer is obvious in that several fractions exist when separated by TREF. The reasons for deviation of the fraction melting points from the predicted values are more subtle. First, the fractions are also heterogeneous in branch content in that they are collected across a 5°C elution temperature range. Second, intramolecular heterogeneity may be implied when fractions of equal branch content as well as branch length exhibit different melting points. For example, two octene copolymer fractions with equal CH_3/1000C content may exhibit different melting points and thus indicate intramolecular heterogeneity.

In terms of product performance, the more important bulk copolymer heterogeneity can be correlated to physical properties of blown film. For this, a continuous mass distribution vs. branch content (elution temperature) relationship is useful (see Figure 5). This distribution can be considered a resin fingerprint when used in combination with molecular weight, molecular weight distribution, and density. Figures 5, 6, and 7 show typical distributions for solution process ethylene/butene, ethylene/hexene, and ethylene/octene copolymers. It is important to note that while variations due to comonomer length exist, variations within a copolymer type are also possible. Figures 7 and 8 show two different distributions for ethylene/octene copolymers.

To illustrate the contribution of branching distribution to film performance, Table II shows a comparison of two ethylene/octene copolymers. The molecular weights, molecular weight distributions, and densities are comparable; however, the branching distributions differ and correspond to Figures 7 and 8 respectively. These data show that a more narrow, homogeneous SCBD results in improved impact strength and optical properties.

Table III shows the effect of comonomer length on selected film properties. These resins have similar molecular weights, molecular weight distributions, and densities. The branching distributions correspond to those shown in Figures 5, 6 and 7. The ethylene/octene and ethylene/hexene copolymers exhibit better tear and impact properties than the ethylene/butene copolymer. This is in spite of the fact that the ethylene/butene copolymer has a more narrow or more homogeneous branching distribution than either the ethylene/hexene or the ethylene/octene copolymers. This serves to illustrate the importance of branch length in determining film performance.

CONCLUSIONS

LLDPE copolymers are characterized by molecular weight, molecular weight distribution, density, branch length, and branch distribution. With molecular weight, molecular weight distribution, and density being equal, branch length is the primary variable responsible for differentiation of the various ethylene/ α-olefin copolymers. Branch distribution is also important,

especially in higher α-olefin copolymers, as a secondary variable in describing product performance. Manipulation of the SCBD can result in subtantial improvements in impact strength and optics of blown films.

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TABLE I

RESIN PHYSICAL PROPERTIES

RESIN	A	B	C	D
Comonomer	Butene-1	Hexene-1	Octene-1	Octene-1
Melt Index (g/10 min)	1.0	1.1	1.0	1.1
I_{10}/I_2	7.8	8.0	7.6	7.5
Density (g/cc)	.921	.921	.922	.922

TABLE II

EFFECT OF SCBD ON BLOWN FILM PROPERTIES*

RESIN	C	D
Dart Impact (g)	193	330
MD Elmendorf Tear (g)	375	450
CD Elmendorf Tear (g)	806	903
Haze (%)	12.4	5.6

TABLE III

EFFECT OF COMONOMER ON BLOWN FILM PROPERTIES*

RESIN	A	B	AVERAGE OF C & D
Dart Impact (g)	121	179	262
MD Elmendorf Tear (g)	137	349	413
CD Elmendorf Tear (g)	378	714	855
Haze (%)	8.4	9.1	9.0

* All films are nominal 1.0 mil and fabricated at a 2.5:1 blow up ratio.

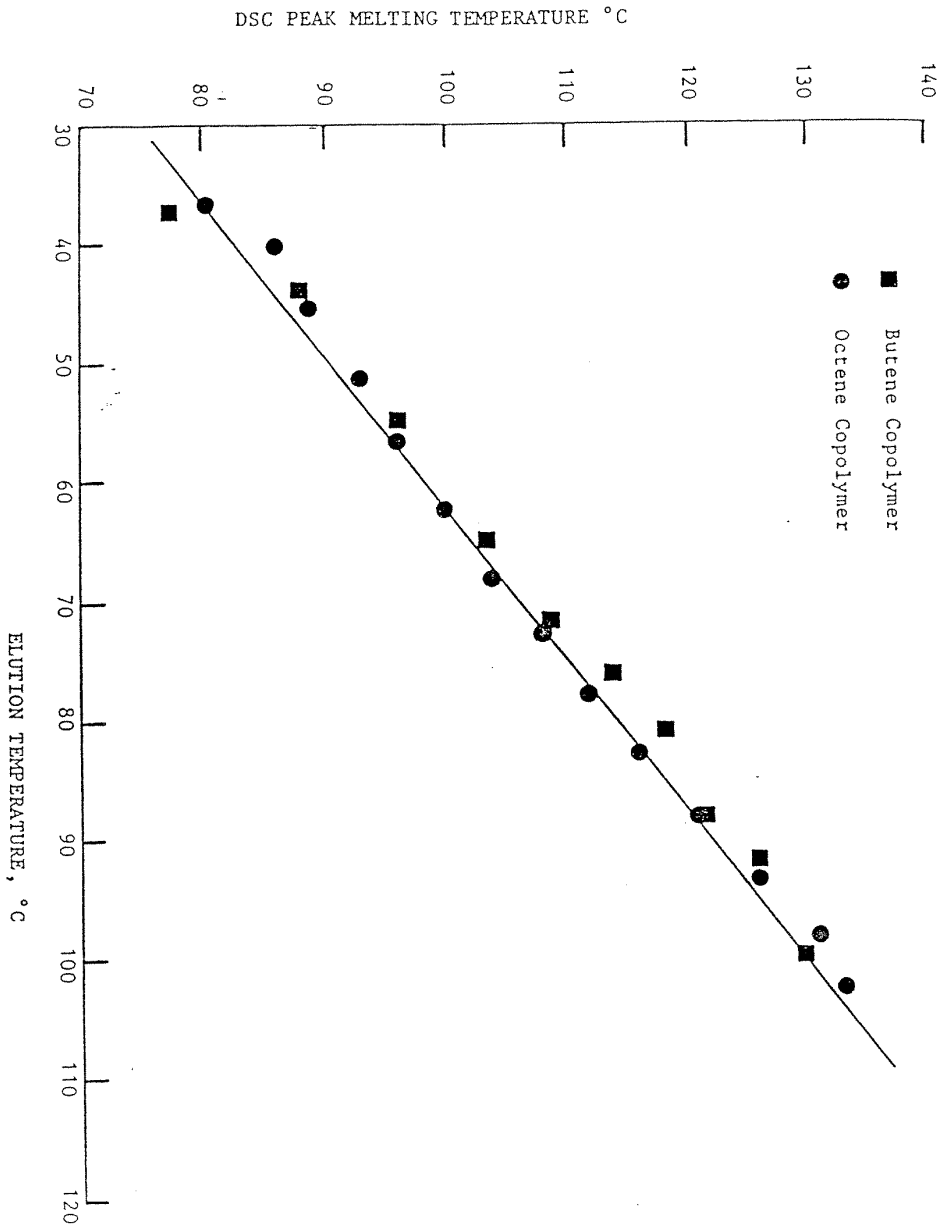
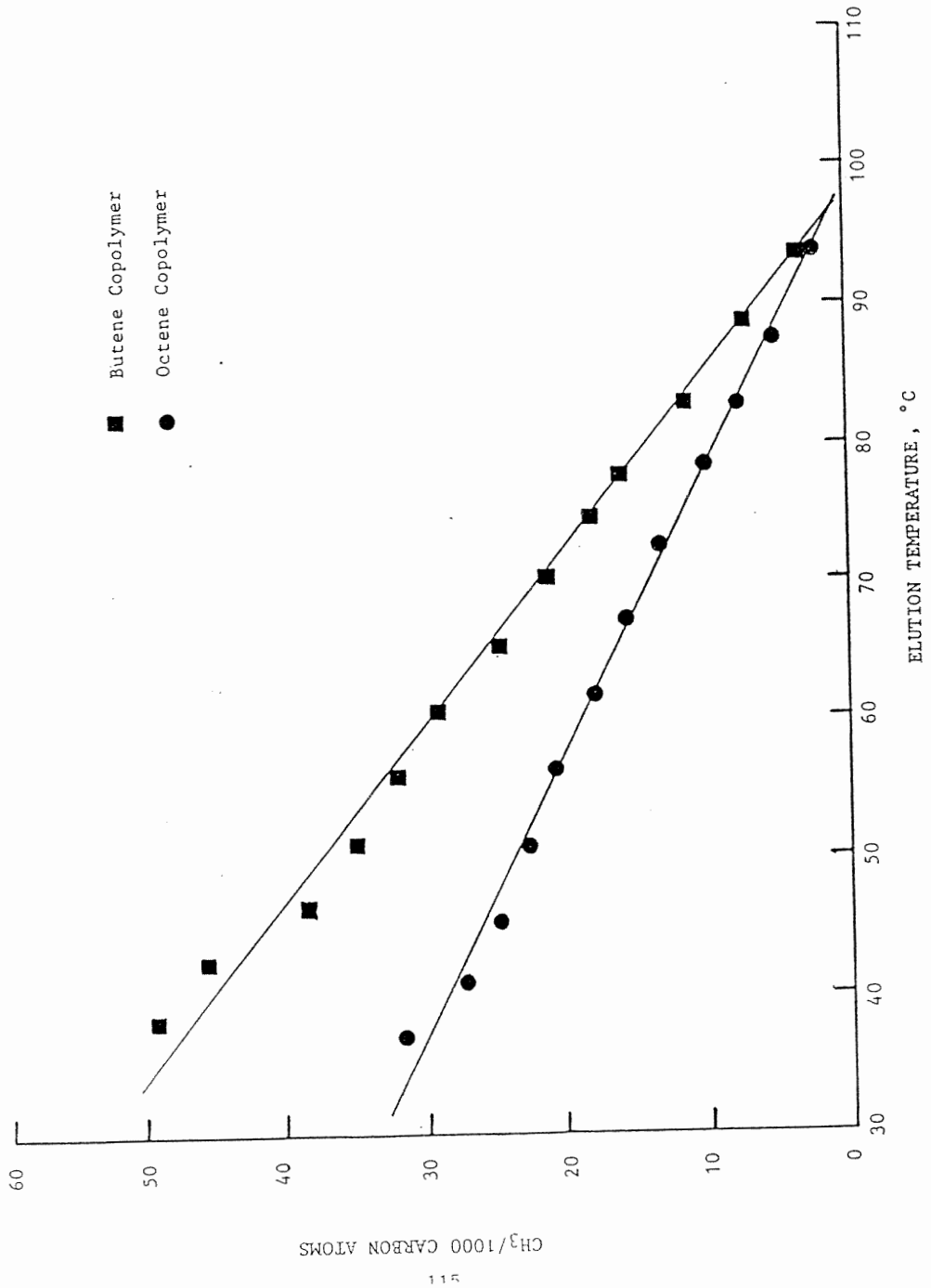


FIGURE 1
MELTING POINT VS. ELUTION TEMPERATURE FOR ETHYLENE/BUTENE AND ETHYLENE/OCTENE COPOLYMER FRACTIONS

FIGURE 2
DEGREE OF SHORT CHAIN BRANCHING VS. ELUTION TEMPERATURE FOR ETHYLENE/BUTENE AND ETHYLENE/OCTENE COPOLYMER FRACTIONS



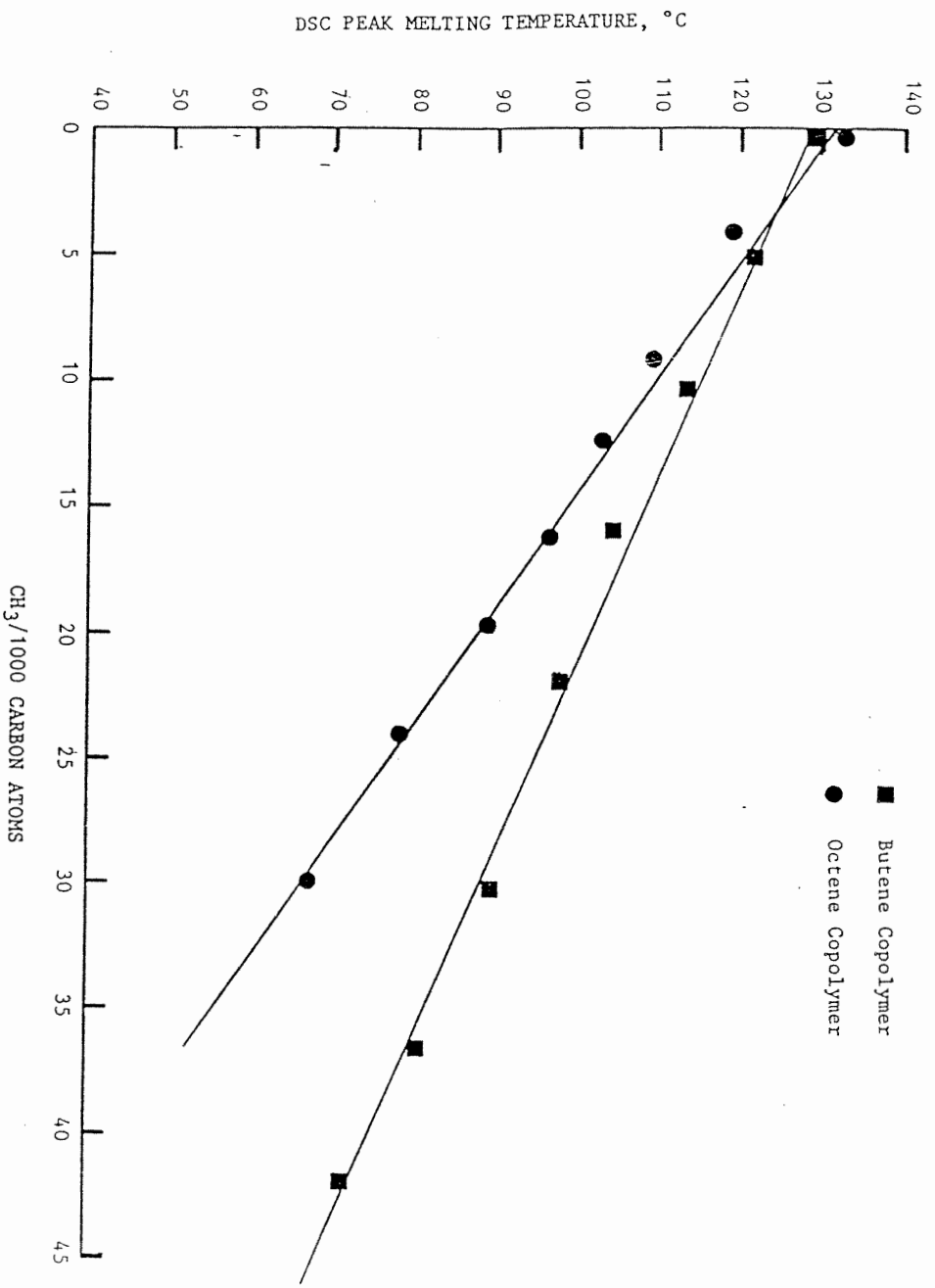


FIGURE 3
DSC MELTING POINT VS. DEGREE OF SHORT CHAIN BRANCHING FOR ETHYLENE/BUTENE AND ETHYLENE/OCTENE COPOLYMER FRACTIONS

FIGURE 4
A COMPARISON OF THEORETICAL AND OBSERVED MELTING POINTS OF
ETHYLENE/BUTENE AND ETHYLENE/OCTENE COPOLYMER FRACTIONS AND WHOLE COPOLYMERS

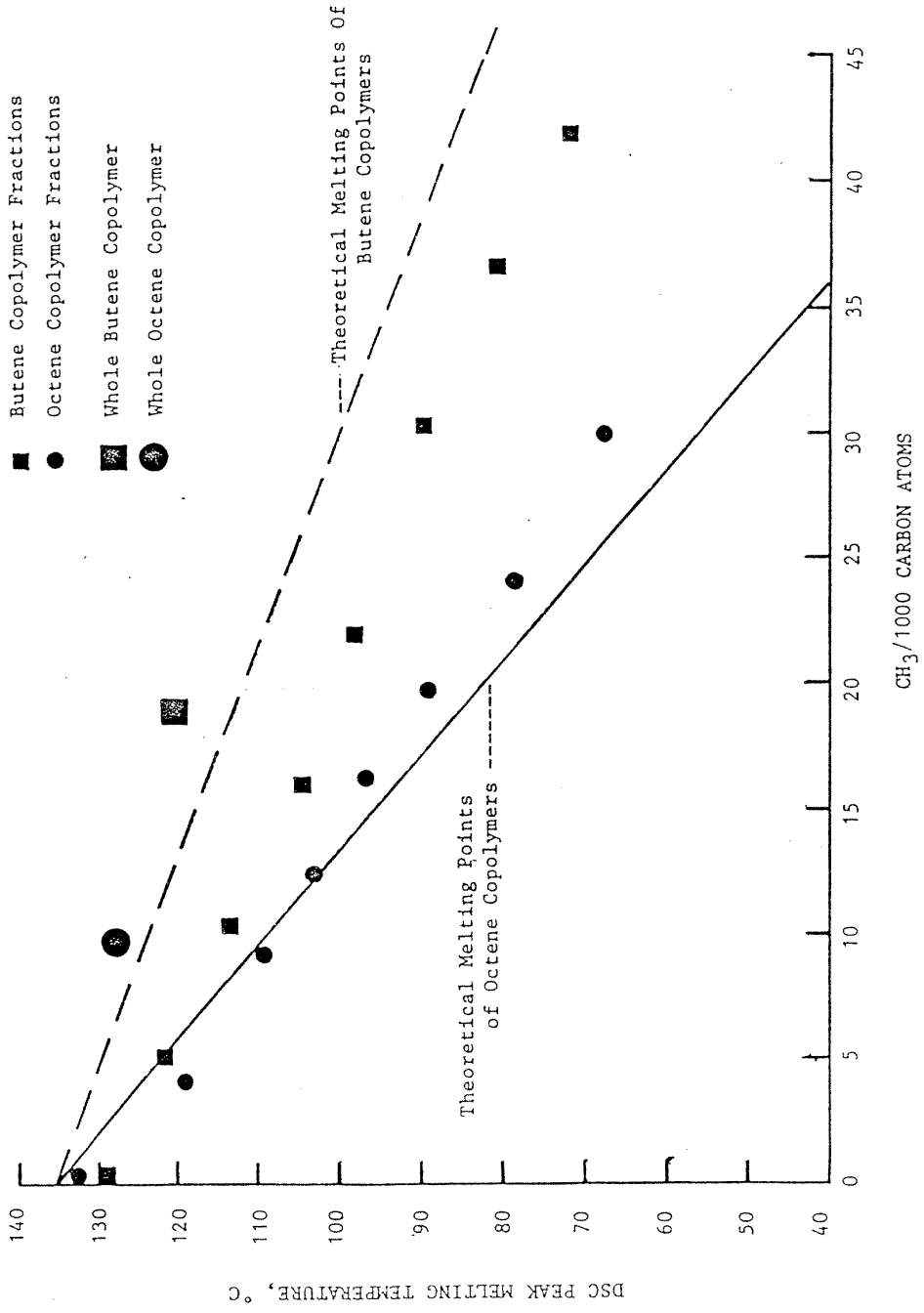


FIGURE 5

SCBD OF LLDPE-A ETHYLENE/BUTENE COPOLYMER

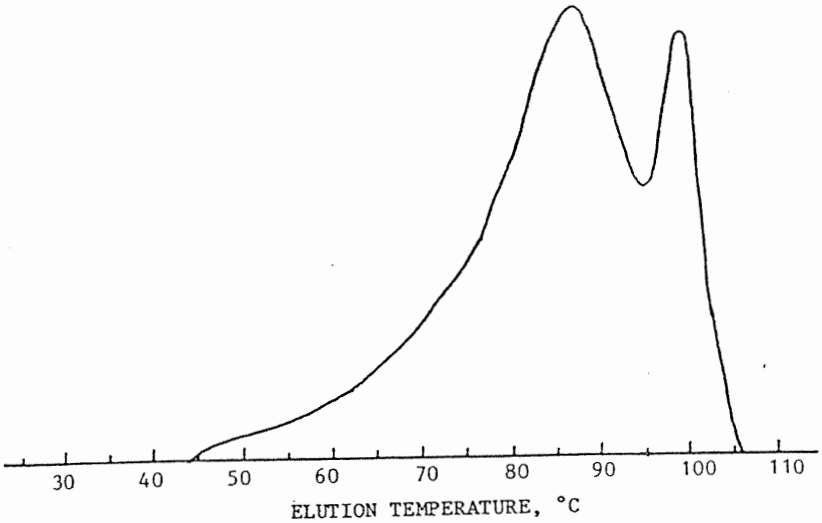


FIGURE 6

SCBD OF LLDPE-B ETHYLENE/HEXENE COPOLYMER

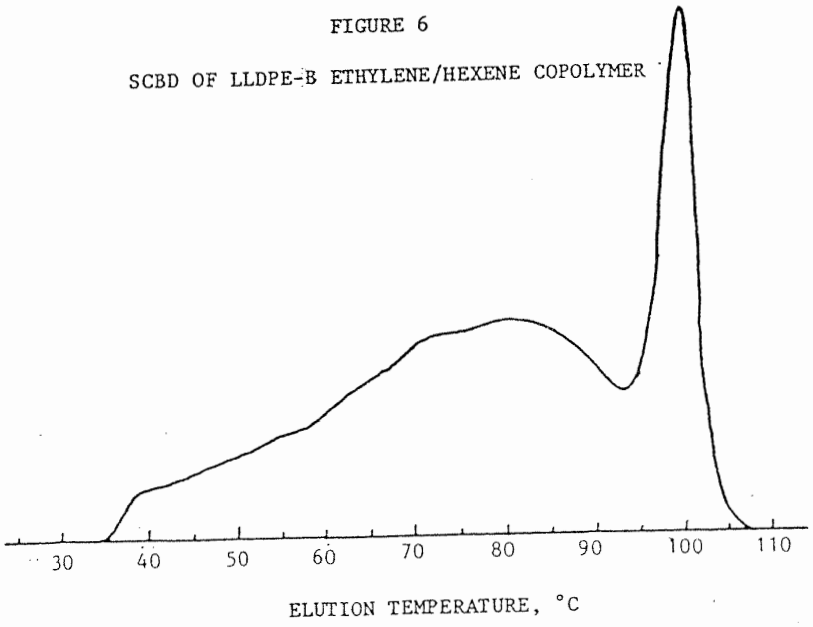


FIGURE 7

SCBD OF LLDPE-C ETHYLENE/OCTENE COPOLYMER

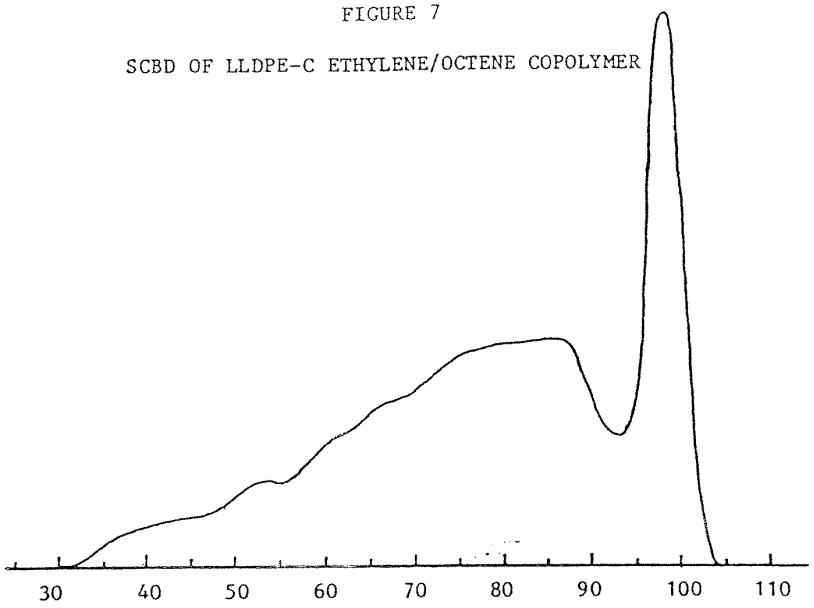
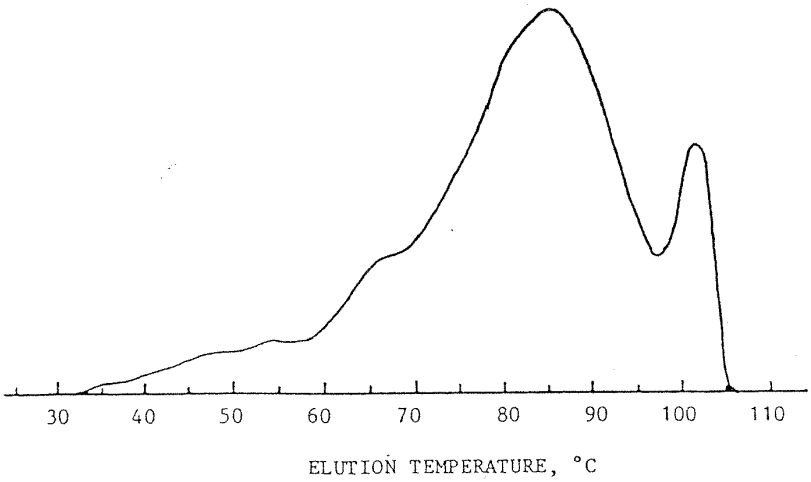


FIGURE 8

SCBD OF LLDPE-D ETHYLENE/OCTENE COPOLYMER



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Determination of Branching Distributions in Polyethylene and Ethylene Copolymers*

L. WILD, T. R. RYLE, D. C. KNOBELOCH, and I. R. PEAT,
Research Division, U.S. Industrial Chemicals Co., 1275 Section Road, Cincinnati, Ohio 45237

Synopsis

A description is given of an analytical temperature-rising elution fractionation (TREF) system for the purpose of determining short-chain branching (SCB) or copolymer distributions in polyethylenes and ethylene copolymers. The system achieves fractionation on the basis of crystallizability and is shown to be very little influenced by molecular weight in the normal high polymer range. Sample preparation by slow cooling from relatively dilute solution followed by continuous elution with a simultaneous and fairly rapid rate of temperature rise proves to be an efficient fractionation process. An on-line detector and data system allows application of a calibration curve to give realistic SCB distribution data in a convenient manner. The potential value of the TREF technique for providing structural information is illustrated by examples which include low-density high-pressure resins made by both tubular and autoclave reactors, high- and low-density resins made by low-pressure processes, and copolymers of ethylene with vinyl acetate and ethyl acrylate.

INTRODUCTION

Polymers are basically heterogeneous materials. Heterogeneity may be exhibited in a number of ways: through a distribution of differing chain lengths, through differences in chemical composition from chain to chain, and through the architecture of the chains as in branched and crosslinked structures. Each form of heterogeneity and the possible combinations within a resin will exert an influence on the behavior and hence the properties of the ultimate product.

Detailed polymer analyses can only be accomplished through the use of fractionation to separate the molecular species according to their differing structures. The most successful and widely used technique is that of size exclusion chromatography (SEC) which, through a size separation, provides a measure of the chain length or molecular weight distribution. Further analysis of species separated by molecular weight usually reveals that they differ in terms of their chemical composition, as outlined in a recent review article.[1] However, it has been demonstrated recently[2] that this approach is not a very effective way of determining composition distributions within most polymers. As suggested by Riess and Callot,[3] what is needed is an additional and complementary fractionation technique which will provide a separation based on composition variation, independent of molecular weight.

For polyethylene resins it is branching which is of particular interest from the point of view of the impact on resin properties and use. Branching, which may be characterized as long chain or short chain, can arise through chain transfer

* Parts of this work were presented at the American Chemical Society Meeting, Chicago, 1977.

Journal of Polymer Science: Polymer Physics Edition, Vol. 20, 441–455 (1982)
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CCC 0098-1273/82/030441-15$01.50

reactions during free-radial polymerization at high pressure or by copolymerization with α-olefins. The overall branching level influences resin properties through its control of crystallinity and morphology. Each branch point and chain end disrupts the local order during crystallization and reduces the degree of crystallinity. Commercial resins are observed to exhibit a wide range of densities (from 0.915 to 0.965 g/mL) as a result of their differing branching levels. Considering the variety of processes used in polyethylene manufacture it would be surprising if variations in molecular weight and long-chain and short-chain branching (SCB) distributions were not common. In particular, SCB distributions are expected to vary significantly and, through the influence on polymer morphology, should exert some control over end-use properties.

Evidence for differences in SCB distributions in commercial resins has been reported.[4,5] However, both these studies considered branching only in terms of its molecular weight dependence and thus, as indicated above,[2] are expected to provide somewhat incomplete indications of the actual branching distributions. The clearest indication of the extent to which SCB may vary within a polyethylene resin comes from the work of Shirayama et al.[6,7] In their studies, a stepwise temperature-rising elution fractionation method similar to the technique described by Desreux and Spiegels,[8] was used to achieve a branching separation. From an experimental standpoint the technique is cumbersome and time consuming, but it does suggest an approach to determining SCB distributions.

In the present article a description is given of efforts to improve the temperature-rising elution fractionation technique so as to provide a more effective and efficient means of determining SCB distributions in polyethylenes and ethylene copolymers. It should be noted that the term "short-chain branching" has been used in connection with the branching distributions reported below, although in a strict sense all branch types influence crystallinity. The purpose of this is to distinguish it from long-chain branching, which, although only normally present in small amount, does have a profound effect on the viscoelastic properties of the polymer melt. This effect is not considered here.

BACKGROUND: PREPARATIVE FRACTIONATION

Fractionation based on crystallizability for the purpose of achieving compositional separation of molecular species has been achieved in a number of studies. For example, fractionation by isothermal crystallization at successively lower temperatures has been reported for both polypropylene oxide[9] and polypropylene.[10] Conversely, fractionation by isothermal dissolution at a series of rising temperatures has been reported for polyethylene[6,7] and polypropylene.[11,12] The work of Shirayama et al.[6] in particular demonstrated clearly that a temperature-rising elution fractionation technique provides a means of determining short-chain branching distributions in low-density polyethylenes. This is because crystallinity in polyethylenes is directly related to the degree of branching.

The temperature-rising approach has a number of advantages for establishing a practical system for determining branching distributions, These include the convenience of elution from a column with an inert support, relative freedom from high polymer concentrations (and thus high viscosities) during elution, and,

in particular, the potential for running under conditions of continuous elution. Automatic operation during the fractionation process can thus be readily achieved.

A temperature-rising elution fractionation (TREF) system has been set up along these lines and successfully operated over a number of years. This preparative TREF system consists of a stainless-steel column 20 × 5 in. in diameter packed with Chromosorb-P support onto which polymer (ca 4 g) is crystallized by slow cooling from a hot xylene solution in a temperature-programmed bath. By continuously eluting the column with xylene at a controlled flow rate (ca 20 mL/min) while applying a programmed rate of temperature rise (8°C/h), separation of molecular species is achieved according to the temperature at which they melt and become soluble. Collecting fractions, weighing, and analyzing for degree of short-chain branching by IR allows one to construct a short-chain branching (or copolymer) distribution for the particular polyethylene analyzed. This system was the proptotype of that used by Bergström and Avela.[13]

Experience with this system suggests that molecular fractionation is achieved mainly during the crystallization step. In practice, slow (natural) cooling overnight has proved quite effective. However, it is found that the temperature at which fractions with a specific degree of branching elute will vary somewhat from resin to resin. As part of efforts to achieve optimum fractionation, experiments were conducted using a more controlled cooling step. In these experiments a resin with a broad SCB distribution was fractionated at a series of constant cooling rates ranging from 20°C/h down to a rate of 0.5°C/h. Optimum fractionation was assumed to have been achieved when the plot of elution temperature versus methyl content became constant, i.e., when no further change was noted on reducing the cooling rate. This condition appeared to be met at ca. 2°C/h. Subsequent analyses of a variety of polyethylene types using slow, controlled cooling (1.5°C/h) indicated that a more consistent elution temperature–methyl content relationship was obtained than was the case using natural cooling. The use of controlled cooling was made part of standard operating procedure.

Much useful data has been generated using this preparative TREF system, which in practice is quite convenient to use. However, the increasing use of SEC combined with TREF for polymer characterization has generated the need for further decrease in the time required to produce distribution data as well as the desire for improved resolution. To meet these needs, a rapid analytical TREF system has been developed. This is described in the following section.

DEVELOPMENT OF ANALYTICAL TREF

Approach

From an operational standpoint the major bottleneck associated with the preparative TREF system is the large number of fractions that need to be processed by filtering, drying, weighing, and pressing films for analysis by infrared. On the other hand, the efficiency of the separation process is probably less than ideal owing to the large size of the column system. The physical dimensions of the system make it difficult to avoid channeling, "dead" spots, and temperature gradients along the length and across the diameter of the column.

These problems have been effectively resolved by a new TREF arrangement

in which the column (and sample) size is reduced considerably and the amount of polymer eluted as a function of temperature is continuously monitored with an in-line detector.

Apparatus

The physical layout of an apparatus for conducting TREF experiments on a small scale, with continuous polymer concentration detection, is shown in Figure 1. A liquid-chromatographic pumping system provides a constant flow of solvent through a stainless-steel column packed with Chromosorb-P support. The column is 5 × 1 in. in diameter and is held in a recirculating oil bath whose temperature is controlled by a temperature programmer. The column is easily removed from the system to allow the crystallization process to be conducted in a separate temperature-programmed bath. In this way, multiple crystallizations can be performed to assure maximum usage of the TREF system. The polymer being eluted from the column as the temperature rises is determined using a differential refractometer maintained above the solubility temperature of the polymer. Heated tubing connects the column to the refractometer to avoid polymer precipitation during the fractionation process. This needs to be temperature controlled just above the temperature of the detector to assure a steady base line. The output from the refractometer and the corresponding column temperature are displayed simultaneously on a two-pen recorder.

Fractionation Procedure

To accommodate the detector, 1,2,4-trichlorobenzene (TCB) is used as solvent for the polyethylene in order to give a suitable refractive index increment. Samples are loaded by injecting 20 mL of a 0.5% solution in hot TCB into the packed column held in the cooling bath at 125°C. A suitable number of loaded columns are cooled simultaneously from 100°C to room temperature at a rate of 1.5°C/h. Individual columns are then loaded into the fractionator at room temperature and eluted with TCB at a flow rate of 4 mL/min and a heating rate of 20°C/h until all polymer has been removed. A steady base line trace is ob-

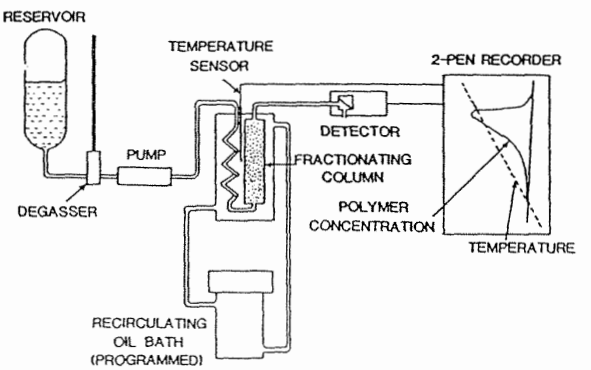


Fig. 1. Analytical temperature-rising elution fractionation system.

tained before starting each run in order to obtain a suitable curve for calculation of the weight distribution as a function of temperature.

Calibration

As with SEC, the use of a detector instead of physical recovery of fractions necessitates the use of a calibration if quantitative data are desired. In the case of TREF, calibration presents a problem in that no standards of narrow branching distribution are available. For this study, standards have been generated using the preparative fractionation system described above. The starting materials were mainly polyethylene resins of similar MI produced in an autoclave reactor at differing, constant temperatures. These were themselves of relatively narrow SCB distribution and covered a density range 0.914–0.933. Some experimental ethylene-butene copolymers were used to produce standards at very low and at higher degrees of branching regions. The preparative TREF was run in a stepwide mode and fractions collected at 4°C temperature increments to get relatively sharp cuts.

The degree of short-chain branching for the fractions was determined on pressed films using a Nicolet 7199 FT-IR with computer subtraction of the polymethylene spectrum. Hexadecane was used as a standard (ASTM D2238-68 method B). From this data and the weight-average peak-position temperature from each TREF trace, a calibration curve of methyl content versus elution temperature has been established (Fig. 2). An excellent linear relationship is observed.

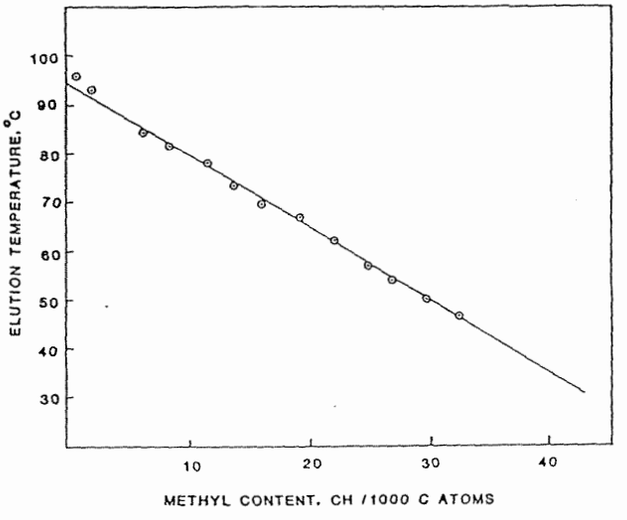


Fig. 2. Calibration curve for analytical TREF system.

Data Handling

Initially, distribution data were obtained by measuring peak heights at 1°C temperature increments. A simple computer program then normalized the data, converted temperature into methyl content through use of the calibration equation, and displayed a curve in the form of the ratio of increments DHT/DN vs N, where HT denotes the normalized cumulative height and N is the methyl content. An average methyl content was also computed to represent the overall degree of SCB of the sample.

Increased sample throughput has made it desirable to automate data acquisition. Presently, the detector output and corresponding values of temperatures are recorded on magnetic tape recorder. The data system is controlled by a Teleray 1061 CRT terminal and the data transmitted by telephone using a Bell 212A modem to an IBM 370 for processing and storage. Data is accessed through the Teleray 1061 or an IBM 3277 terminal, and computed data and distribution curves are printed on-site at a Data 100 terminal. Through recall of stored data, multiplots of up to five distribution curves can be generated using a Calcomp model 1012 plotter.

On occasion, when determining the SCB distributions for polymers with significant amount of material with very low levels of branching, a small part of the computed curve extends below a methyl content of zero. This is due mainly to a slight upturn in the calibration curve in the low-methyl-content region which is not fully taken into account by the linear form of the calibration equation used. In order that all the data be represented on the curve plots, negative values for methyl content have been allowed. However, when computing average methyl contents from the SCB data, negative values of methyl content are assumed to be equal to zero.

RESULTS AND DISCUSSION

The major thrust of the work reported here is to develop a fractionation system which is easy to operate and provides a reasonably high output of data. However, the practical value of the data is very much dependent on the quality of the fractionation achieved. It is important to demonstrate that under the conditions used, fractionation does in fact take place according to the degree of short-chain branching and is sufficiently independent of molecular weight influences. Also, in order to use a calibration to calculate degree of SCB in any meaningful way, the separation temperature of a given molecular species should not be influenced by the presence or absence of other polymer molecules. These aspects are addressed below.

Influence of Molecular Weight

The possibility of a strong molecular weight dependence coming into play during fractionation by crystallization is very real, judging by the studies of Pennings.[14] He has clearly demonstrated that during crystallization of linear polyethylene from solution under a variety of conditions, species of like molecular weight tend to cocrystallize, causing some fractionation to occur. However, no evidence for any serious molecular weight dependence has been noted during the present TREF studies.

The fact that a good calibration curve was obtained using fractionated samples (Fig. 2) provides a convincing indication that molecular weight is not an overriding influence. Although no systematic molecular weight measurements have been made on these standards, it is expected that they are in the range 20,000–100,000. Certainly there are no extremely high- or low-molecular-weight samples among the calibration standards. Any strong influence of molecular weight would be seen as a tendency to "bunch up," along the degree of branching scale and to show a poor correlation coefficient between degree of SCB and separation temperature. The actual calibration curve obtained has an excellent correlation coefficient of 0.979 based on a linear least-squares fit of the data. This appears to be consistent with the relation of Flory,[15] in which the heat of fusion or degree of crystallinity varies inversely as the number of noncrystallizable units per unit chain length (i.e., comonomer content).

In a more direct test of possible molecular weight dependence, a series of narrow-molecular-weight-distribution (MWD) fractions of linear polyethylene covering a wide range were analyzed using the TREF system. The data obtained are shown in Figure 3. Here it is clearly seen that in the lower-molecular-weight region (<10,000), the temperature of separation is significantly and increasingly molecular weight dependent. This effect was not unexpected as it is well known that chain ends act as noncrystallizable units. From the point of view of the TREF system this influence of molecular weight could present some difficulty in interpreting the data. However, if we consider the chain end to be acting as though it were a short-chain branch and counted in the total branching measurement, the TREF data take the form shown in Figure 4. It is only when molecular weight gets down into the region of 1000 and below that significant deviation from the calibration line is noted. This presents no problem with the commercial polyethylenes normally encountered.

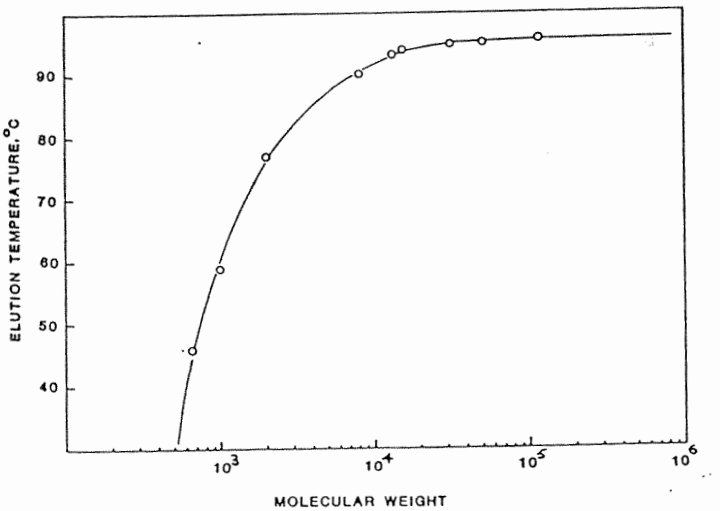


Fig. 3. Molecular weight dependence of elution temperature for linear polyethylene fractions of narrow MWD.

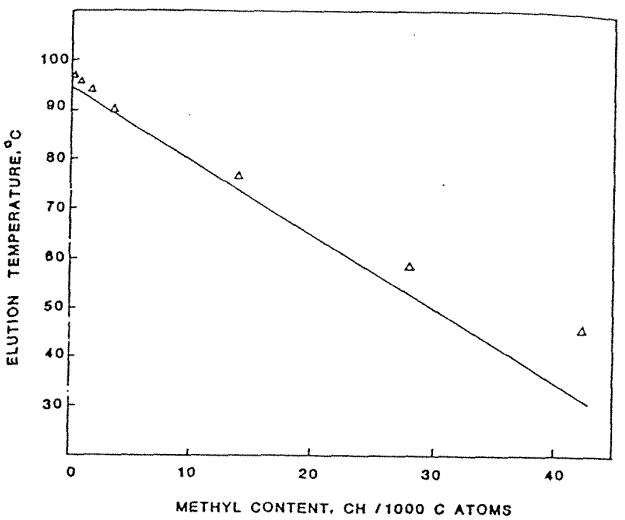


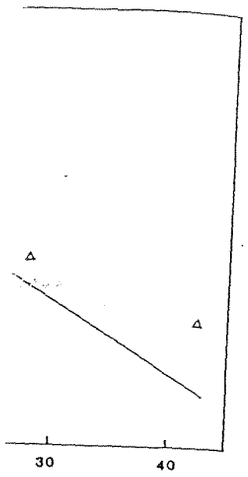
Fig. 4. Comparison of elution temperatures for linear polyethylene fractions with the calibration curve obtained using branched fractions from TREF.

By extrapolating the data in Figure 3 one would predict that material with a molecular weight below 500 will remain in solution at room temperature. An attempt to run TREF on a sample of dotriacontane ($C_{32}H_{66}$) proved unsuccessful owing to the lack of any crystallization from solution, confirming the presence of a lower-molecular-weight limit for the present TREF system. Conversely, one would expect highly branched material, regardless of its molecular weight, to remain in solution when the degree of branching exceeds ca 48 methyls per 1000 C atoms.

Cocrystallization Effects

Fractionated samples have been used for calibrating the TREF system. Polymer samples to be analyzed by TREF will presumably contain a much broader distribution of molecular species of differing degrees of SCB that do the calibration standards. In order to apply the calibration and obtain realistic data, the temperature at which any molecule elutes should not be influenced by the presence of other molecules with differing structure. Any tendency for molecules to cocrystallize with unlike species will lead to a loss in fractionation efficiency.

Two experiments have been performed in attempts to determine the extent to which molecular species behave independently during the fractionation process. The first approach involves a comparison of the fractionation data for a series of three individual fractions with that obtained when they are allowed to crystallize from a solution containing all three fractions in equal parts. Loss of resolution or shift in their elution temperatures would indicate intermolecular interference during the crystallization or dissolution steps. The three samples



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chosen were (I) a linear polyethylene fraction (M_w 32,000) from NBS and fractions from high-pressure low-density polyethylenes with methyl contents of 6.2 (II) and 19.1 (III) methyls/1000 C atoms. The fractionation data obtained are shown in Figure 5 and indicate that excellent separation has been achieved with no significant shifts in peak temperature. Also, only slightly more overlap of curve "tails" is observed in the three-part blend beyond that which would be expected from the individual fractionations. In this instance, cocrystallization effects appear to be negligible.

A second method of demonstrating that the new TREF system provides realistic SCB distribution data is through a comparison of total degree of branching obtained from fractionation data of broad-distribution resins with that measured for the whole polymer by the infrared technique. Data obtained for a wide variety of resin types is shown in Table I. Good agreement is seen between measured and computed values for methyl content, suggesting that the calibration line is applicable to whole polymers of broad SCB distribution with very little distortion. Thus, under the conditions used in these experiments, there is no evidence that the elution temperature of a particular molecular species is significantly influenced by other molecules present in the sample.

The data presented here does not preclude the possibility that cocrystallization may influence the separation process under other conditions and with other sample types. Evidence has been presented[13] which suggests that where "composite" molecules exist with chain segments having differing crystallizabilities, the molecules' behavior may be dominated by the more crystallizable parts. In the ultimate situation in which high-molecular-weight blocks of polyethylene units are present in a copolymer, this type of behavior is clearly

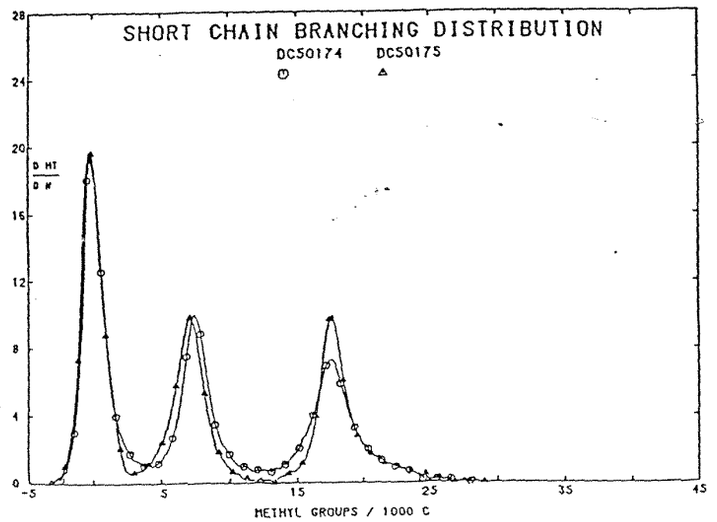

Fig. 5. Comparison of SCB distributions obtained for a three-part blend of samples I, II, and III (⊙) with that obtained by individual fractionation of the three samples (△).

TABLE I
Comparison of Infrared Methyl Content Data With that Computed from TREF

Resin	SCBD	CH_3/1000 carbon atoms Infrared	TREF
A	narrow	1.7	1.8
B	narrow	9.8	9.5
C	narrow	15.7	15.1
D	medium	13.6	14.1
E	medium	18.8	19.6
F	medium	19.7	18.6
G	broad	8.1	8.6
H	broad	13.1	13.4
I	broad	14.0	13.7

expected. However, in the studies presented here no evidence has emerged to indicate any influence of composite structures.

ANALYSIS OF POLYETHYLENE RESINS

The potential usefulness of the TREF method for determining short-chain branching or copolymer distributions can be best illustrated by looking at the typical kinds of distributions observed in polyethylene resins made by differing processes. For example, in Figure 6, a typical tubular-reactor high-pressure polyethylene is seen to exhibit a SCB distribution that is significantly broader than that of a resin produced by an autoclave reactor. This reflects the differences in polymerization conditions associated with the two reactor types.

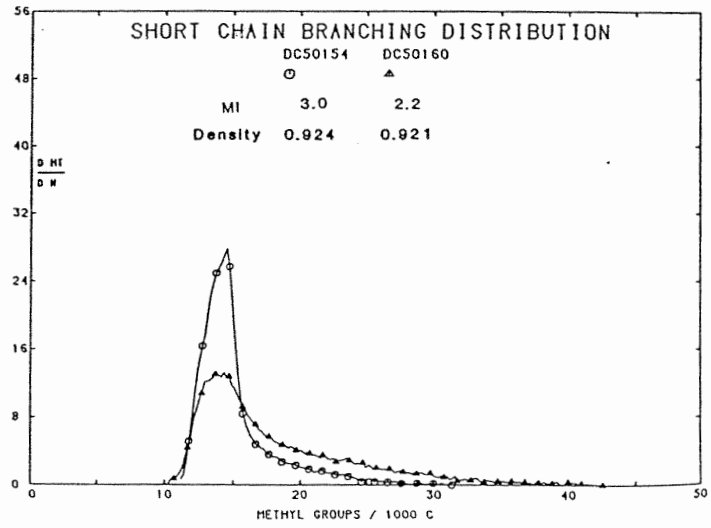

Fig. 6. Comparison of the SCB distribution of an autoclave reactor polyethylene (⊙) (MI 3.0, density 0.924) with that for a typical polyethylene from a tubular reactor (△) (MI 2.2, density 0.921).

omputed from TREF

g/1000 carbon atoms d	TREF
	1.8
	9.5
	15.1
	14.1
	19.6
	18.6
	8.6
	13.4
	13.7

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RESINS

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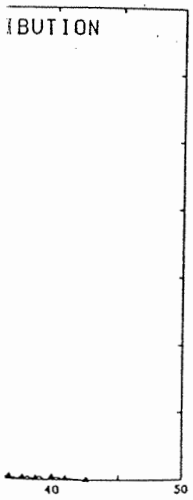

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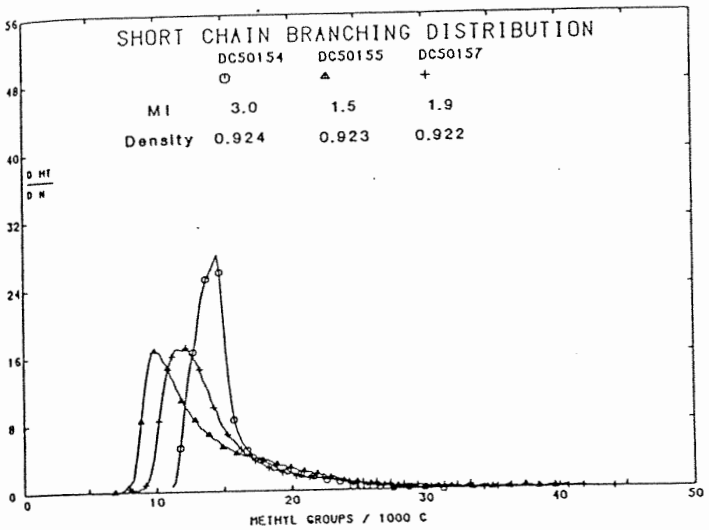

Fig. 7. SCB distributions for resins made in an autoclave reactor under differing operating conditions: (⊙) MI 3.0, density 0.924; (△) MI 1.5, density 0.923; (+) MI 1.9, density 0.922.

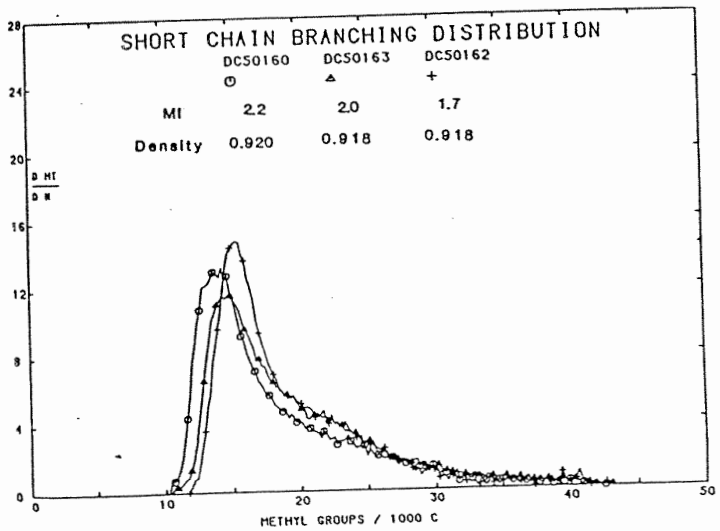

Fig. 8. Effect of changing reactor conditions on SCB distributions of tubular reactor resins: (⊙) MI 2.2, density 0.920; (△) MI 2.0, density 0.918; (+) MI 1.7, density 0.918.

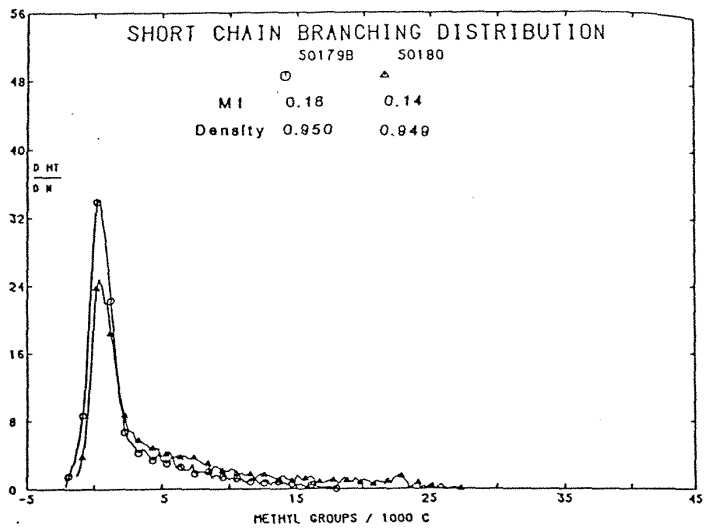

Fig. 9. Comparison of SCB distributions of ethylene-butene-1 copolymers made by differing catalyst systems: (⊙) MI 0.18, density 0.950; (▲) MI 0.14, density 0.949.

Changes in polymerization conditions can also influence the SCB distributions observed for resins produced in the same reactor. Thus the more sophisticated reactor technology of today, particularly that associated with the autoclave process, produces resins with widely differing SCB distributions which in turn exert their influence on resin performance. This can be seen in Figure 7. Tubular-reactor resins, although they tend to be moderately broad SCB distribution, also exhibit notable distribution differences (Fig. 8).

TREF analyses have also been performed on resins produced at lower pressures by copolymerization of ethylene with butene-1. The higher-density materials exhibit SCB curves like those shown in Figure 9. These are characterized by a very distinctive sharp peak of low copolymer content together with a broad, higher branching tail. Here also, differences are observed between resins produced by differing catalyst systems. The differences are expected to influence the balance of resin properties, particularly those such as stiffness versus stress-crack relationships which are morphology dependent. At high levels of comonomer one obtains linear low-density polyethylenes, which are becoming increasingly important commercially. As shown in Figure 10, these materials exhibit extremely wide comonomer distributions, while still showing the presence of a peak associated with very low comonomer levels. It is clear that the high stretchability and stiffness characteristics of these products are related to their broad SCB distributions and the presence of material of high crystallinity. The differences noted in the distributions shown in Figure 10 probably result from the differing processes used to produce the two resins.

Some ethylene copolymers with other comonomers such as vinyl acetate and