EXHIBIT Z

IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

THE DOW CHEMICAL COMPANY, Plaintiff, v. NOVA CHEMICALS CORPORATION (CANADA), and NOVA CHEMICALS INC. (DELAWARE), Defendants.	)	C.A. No. 05-737 (JJF) **JURY TRIAL DEMANDED**

SUPPLEMENTAL DECLARATION OF DR. CHARLES STANLEY SPEED IN SUPPORT OF NOVA'S RESPONSIVE BRIEF ON CLAIM CONSTRUCTION

Dr. Charles Stanley Speed, being first duly sworn upon oath, states as follows:

1. I am the same Charles Stanley Speed that submitted a declaration in support of NOVA's Opening Brief on Claim Construction.

2. I have reviewed the Declaration of Joao B. P. Soares, Ph.D. submitted by Dow in support of its opening Markman brief, and disagree with the conclusions of Dr. Soares.

3. In particular, I disagree with Dr. Soares that it is "well known" that the 98°C TREF peak in Dowlex 2045 contains ethylene molecules that have a few short chain branches. Dr. Soares also does not refer to any citations or publications to support this assertion.

4. Contrary to what Dr. Soares asserts is well known, documents from the file history of Dow's patents-in-suit indicate that a TREF peak at 98°C can correspond to polymer having no short chain branching. These references from the file history thus demonstrate that the 98°C Dowlex 2045 fraction may be linear, *i.e.*, "has neither branched nor highly branched fractions, but is linear," as described in the patents-in-suit. (*See, e.g.*, '053 patent, col. 7, ll. 43-45, col. 8, ll. 4-7.)

5. The article entitled "Determination of Branching Distributions in Polyethylene and Ethylene Copolymers" by Wild et al, J. POLYMER SCIENCE, POLY. PHYS. ED., Vol. 20, 441-455 (1982) ("the Wild article," attached as Exh. A), is an authoritative and widely cited TREF reference cited in the '053 patent at col. 3, lines 44-45 and the '023 patent at col. 3, lines 45-46. The Wild article includes calibration curves correlating the methyl

content (also represented as the number of methyls (CH_3) per 1000 carbon atoms) with measured TREF elution temperatures. As explained by Wild, the methyl content is a measure of the overall degree of short chain branching of the sample, with zero CH_3/1000 carbon atoms (*i.e.*, those methyls associated with short chain branching, not including any end group contributions) corresponding to zero short chain branching.[1] Figure 2 of the Wild article illustrates the case where TREF elution temperatures above approximately 95°C correspond to zero methyl content, or in other words, polymers having **no** short chain branching. (*See* Exh. A, Figure 2.)

6. Another reference I reviewed is an article by L.D. Cady of the Dow Chemical Company ("the Cady article") entitled "The Role of Comonomer Type and Distribution in LLDPE Product Performance." (Attached as Exh. B.) I understand this article was submitted to the Patent Office by Dow's attorneys during the prosecution of the patents-in-suit. Figure 2 of the Cady article illustrates another TREF calibration where polymer fractions lacking any short chain branching elute at temperatures of about 98°C or higher.

7. Thus the data reported in both the Wild article and the Cady article, which are both a part of the file history of the patents-in-suit, clearly indicate that fractions eluting in the 98°C temperature region could be purely linear homopolymer, *i.e.*, no short chain branching.

8. I have also reviewed Dow's opening brief, in particular its position regarding the inclusion of a CDBI value in the definition of "homogeneously branched linear ethylene/α-olefin interpolymer." I disagree with Dow's position that a CDBI value should not be included as part of the definition of "homogeneously branched." Contrary to Dow's position, CDBI is useful as a quantitative tool for characterizing properties of polymers, as described in the patents-in-suit. (*See, e.g.*, '053 patent, col. 3, ll. 35-51.)

9. A particular CDBI value is a measure of the intermolecular short chain branching distribution of a polymer, with a lower CDBI value corresponding to a broader (*i.e.*, more heterogeneous) branching distribution. The lowest CDBI value for a homogeneously branched ethylene/α-olefin interpolymer, consistent with the patents-in-suit and the practice in the art, would be a CDBI value of greater than or equal to 30%. I am not aware of any definition of homogeneously branched that includes a CDBI of less than 30%, and believe that a definition for "homogeneously branched" that encompasses polymers having CDBI values of less than 30% would be inconsistent with the practice in the art and Dow's practice as well.

10. For example, Dow's U.S. Patent No. 5,395,471, by Lai et al. (an inventor of the patents-in-suit) equates the term homogeneously branched with copolymers having a CDBI greater than or equal to 30% (col. 6, lines 23-28) and Dow's U.S. Patent No. 5,582,923

[1] More specifically, in the case that the number of methyls per 1000 carbons includes end group methyls not corresponding to short chain branching, as the number of short chain branches decreases to zero, the number of short chain branches reaches zero prior to the number of methyls per 1000 carbons arriving at zero.

similarly characterizes homogeneously branched ethylene polymers, with that term "used in the conventional sense," as having a CDBI greater than or equal to 30 % (col. 7, l. 7 - col. 8, l. 5). Additionally, Dow's U.S. Patent No. 6,015,617, by Markovich and Chum et al. (inventors of the patents-in-suit) discloses that homogeneously branched ethylene polymers "typically" have a CDBI of greater than 30%. (Col. 6, lines 7-9).[2]

11. Thus, CDBI is an appropriate and common measure in the art to characterize branching distribution and the broadest definition of homogeneously branched ethylene/α-olefin interpolymer, consistent with the patents-in-suit and the art generally, would specify a CDBI of greater than or equal to 30%.

Further Affiant Sayeth Not.

Charles Stanley Speed

Dated: August 26, 2008

[2] While these references are dated after the April 1993 filing date of the patents-in-suit, I believe they are nonetheless reflective of the use of the terms in 1993, as there was no fundamental change in the meaning of the terms from 1993 through 1998.

EXHIBIT A

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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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,

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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

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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-

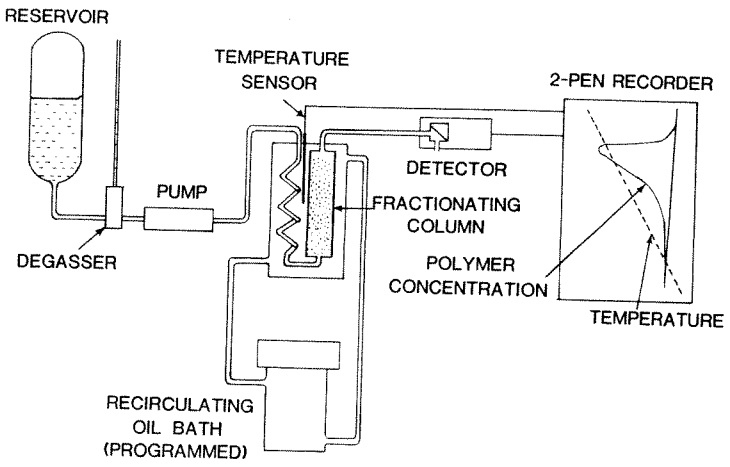


Fig. 1. Analytical temperature-rising elution fractionation system.

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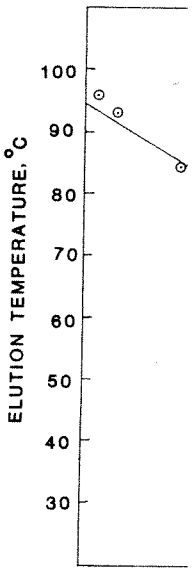


Fig. 2.

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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.

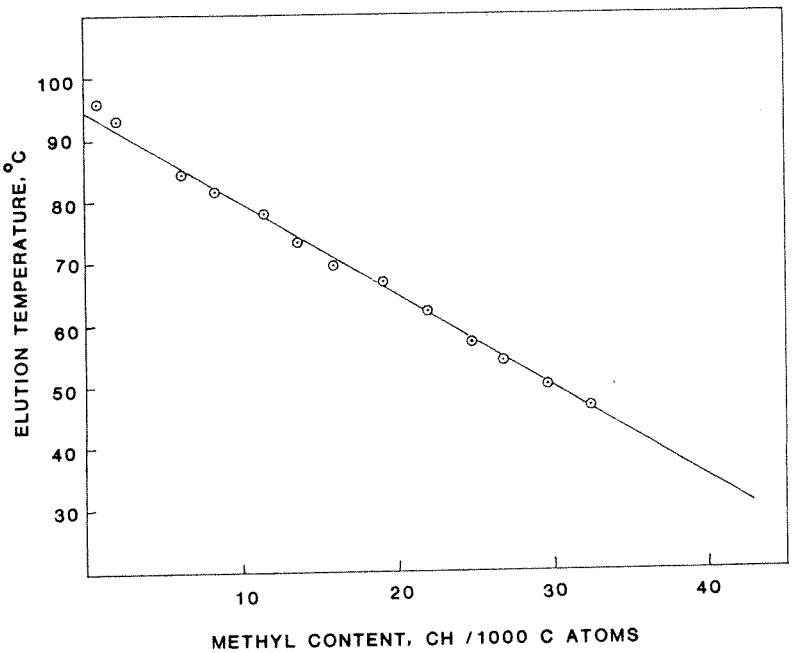


Fig. 2. Calibration curve for analytical TREF system.

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.

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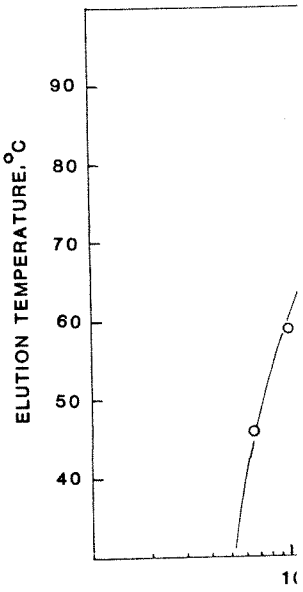


Fig. 3. Molecular weight dep
of narrow MWD.

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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.

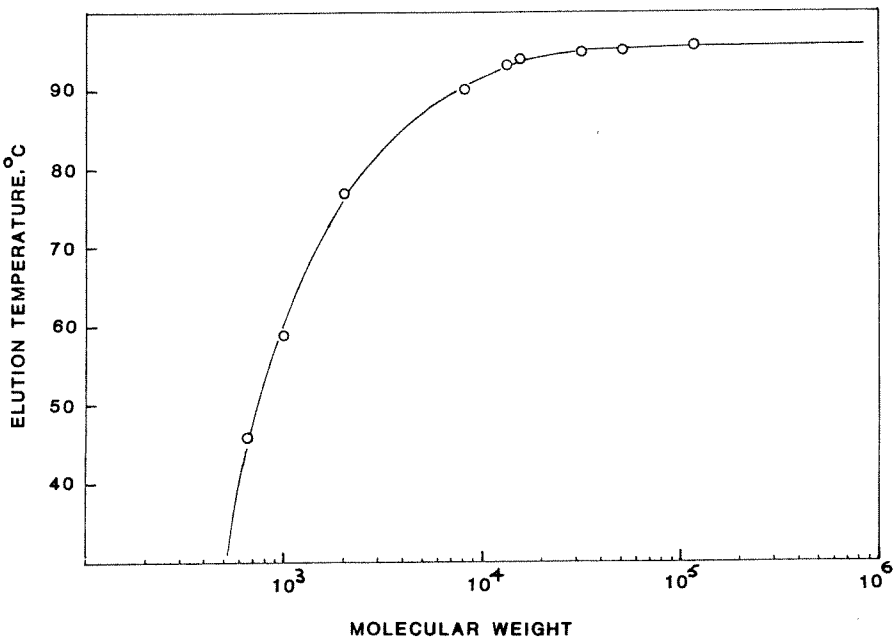


Fig. 3. Molecular weight dependence of elution temperature for linear polyethylene fractions of narrow MWD.

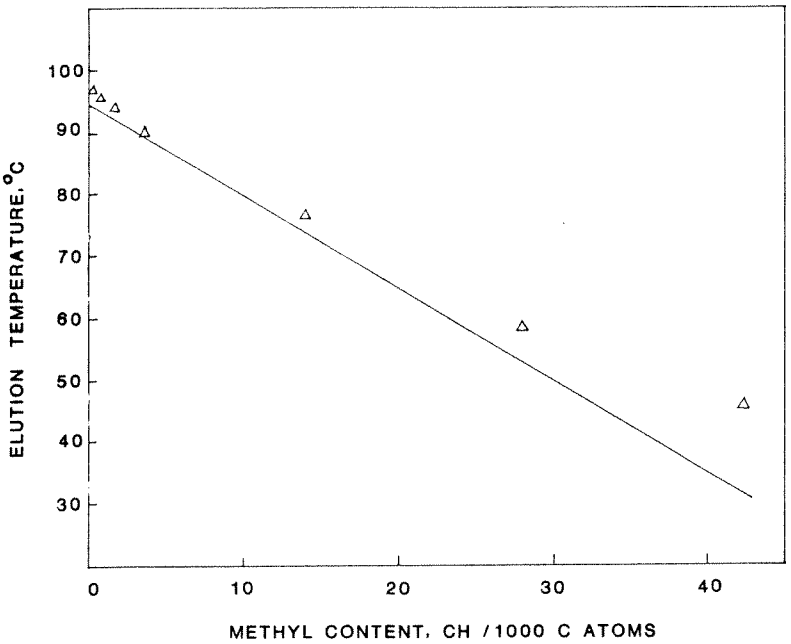


Fig. 4. Comparison of elution temperatures for linear polyethylene fractions with the calibration curve obtained using branched fractions from TREF.

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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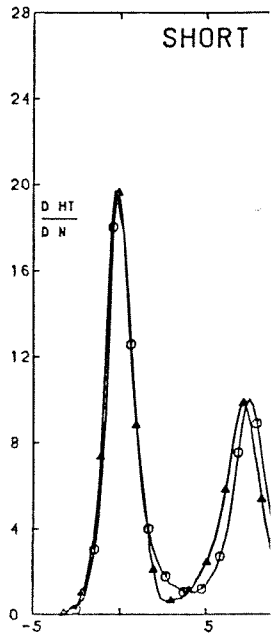


Fig. 5. Comparison of SCB
(⊙) with that obtained by ind

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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

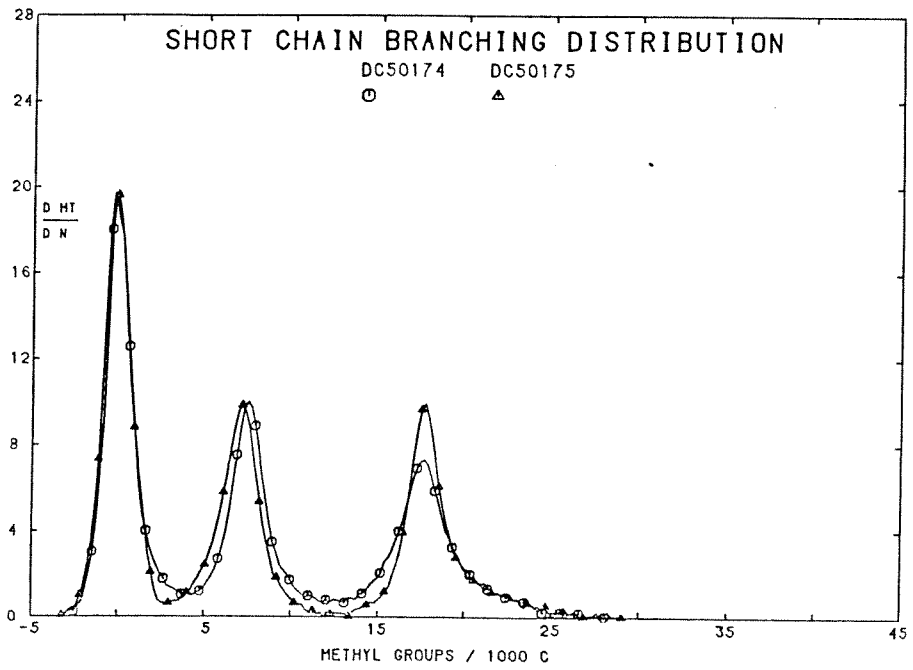


Fig. 5. Comparison of SCB distributions obtained for a three-part blend of samples I, II, and III (⊙) with that obtained by individual fractionation of the three samples (△).

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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.

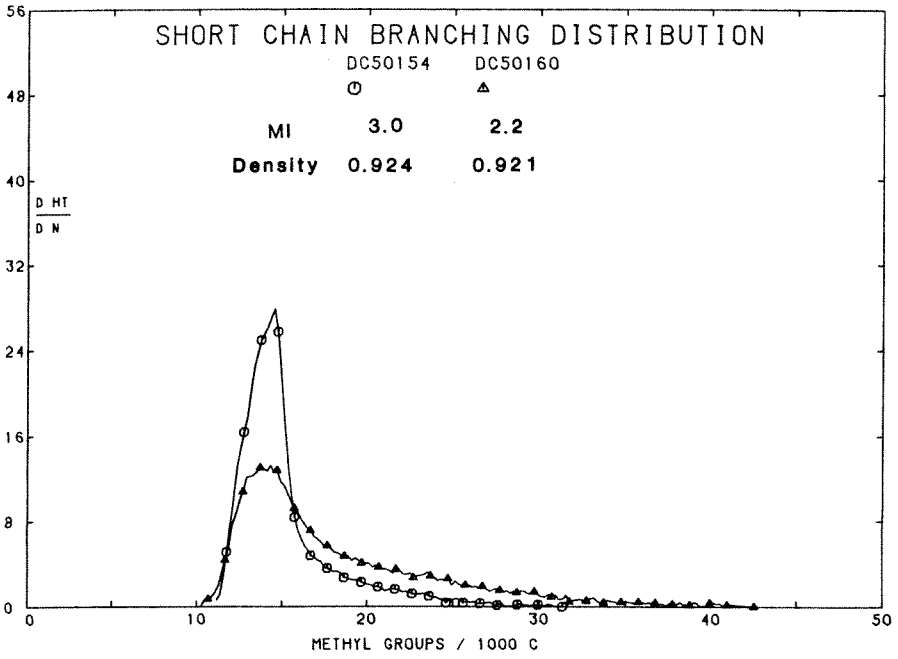


Fig. 6. Comparison of the SCB distribution of an autoclave reactor polyethylene (⊙) (MI 3.0, density 0.924) with that for a typical polyethylene from a tubular reactor (△) (MI 2.2, density 0.921).

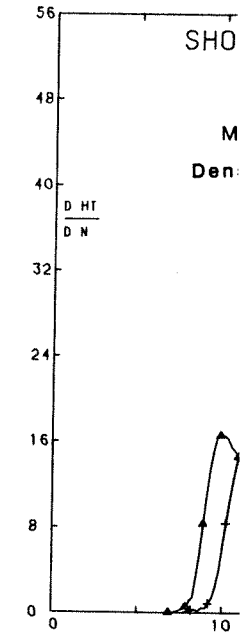


Fig. 7. SCB distributi
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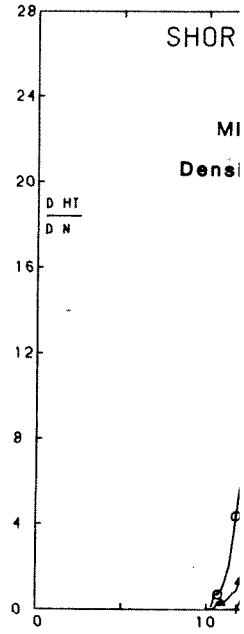


Fig. 8. Effect of changir
MI 2.2, density 0.920; (△)

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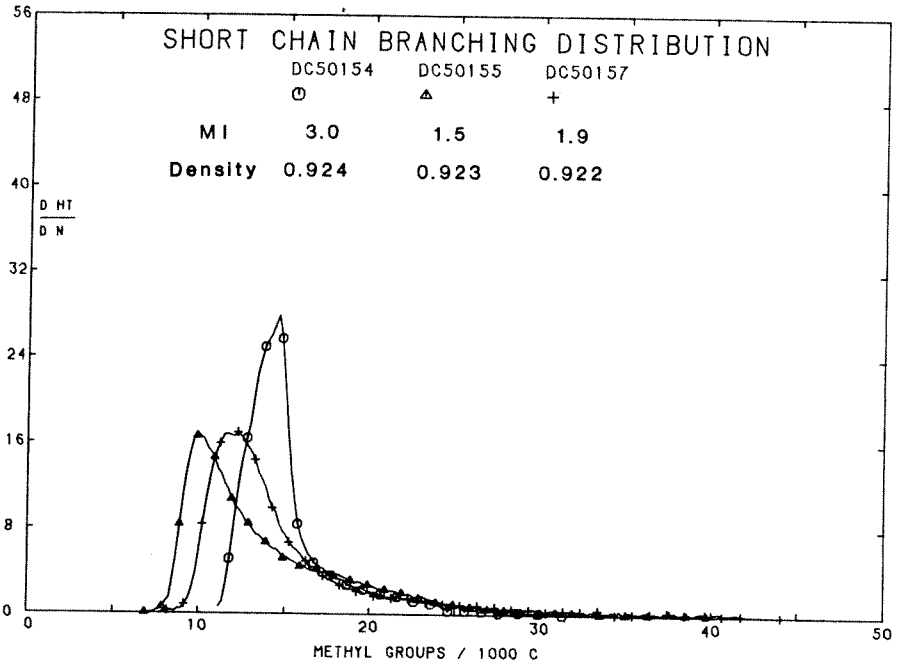


Fig. 7. SCB distributions for resins made in an autoclave reactor under differing operating conditions: (⊙) MI 3.0, density 0.924; (△) MI 1.5, density 0.923; (+) MI 1.9, density 0.922.

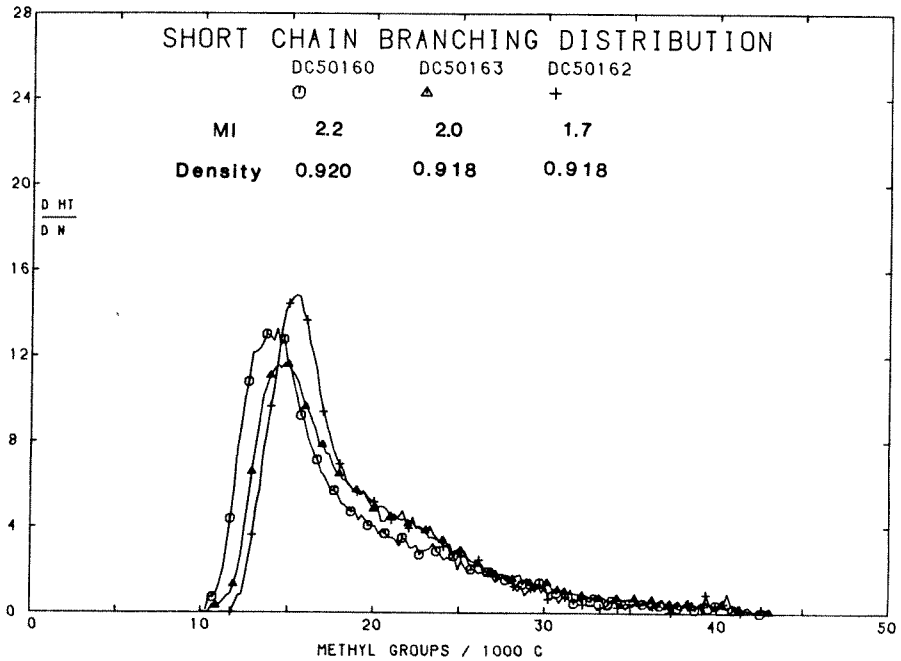


Fig. 8. Effect of changing reactor conditions on SCB distributions of tubular reactor resins: (⊙) MI 2.2, density 0.920; (△) MI 2.0, density 0.918; (+) MI 1.7, density 0.918.

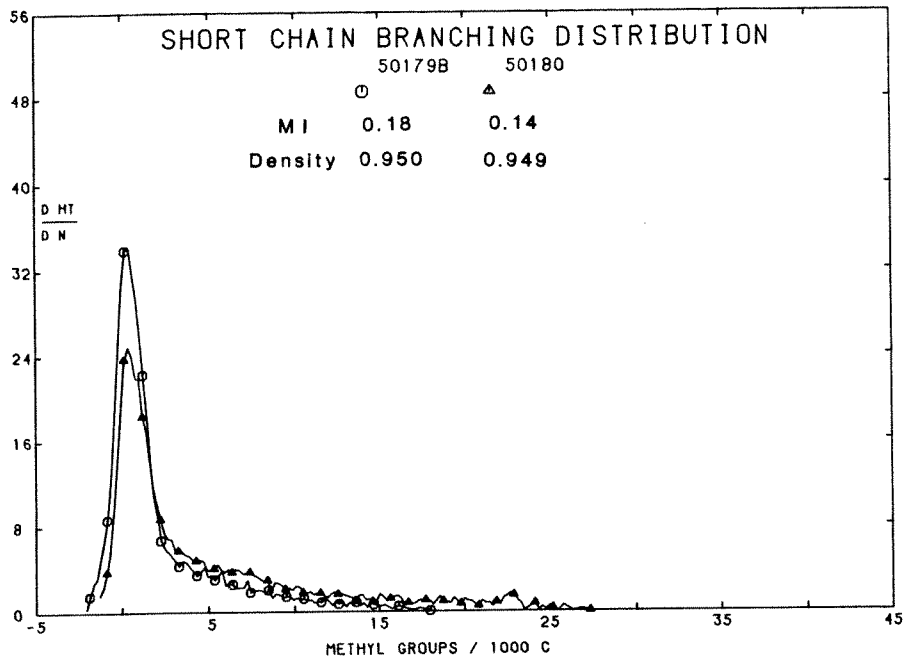


Fig. 9. Comparison of SCB distributions of ethylene-butene-1 copolymers made by differing catalyst systems: (⊙) MI 0.18, density 0.950; (△) MI 0.14, density 0.949.

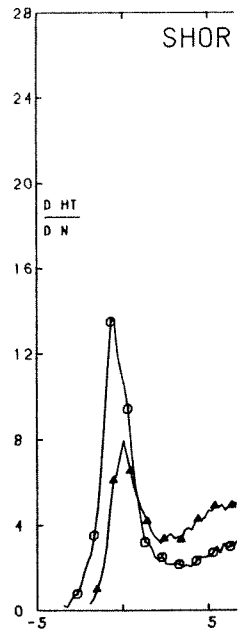


Fig. 10. SCB distributions
1.2, density 0.919; (△) MI

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

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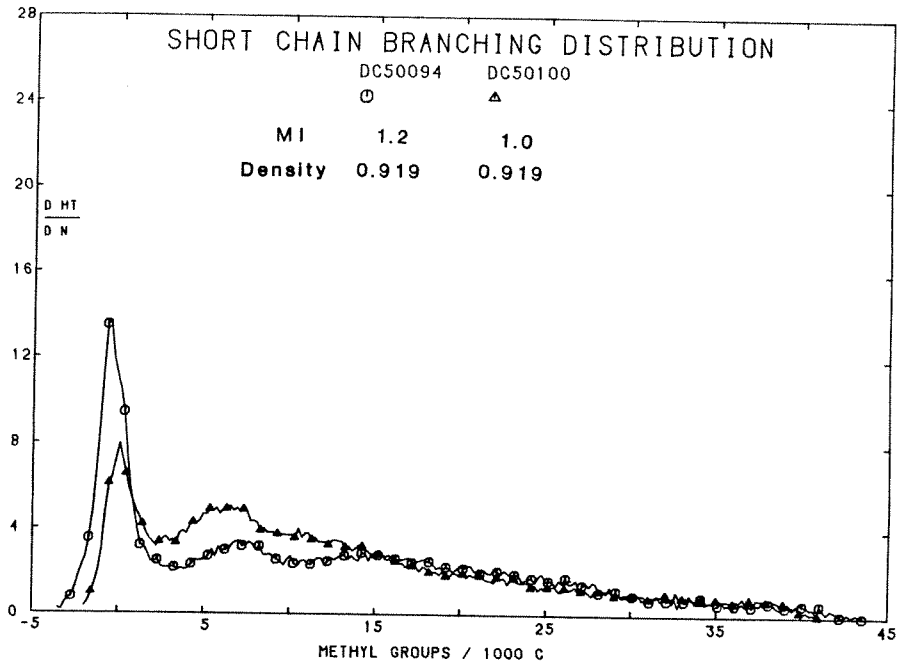


Fig. 10. SCB distributions for two commercial LLDPE resins made by different processes: (⊙) MI 1.2, density 0.919; (△) MI 1.0, density 0.919.

ethyl acrylate are also semicrystalline and can be analyzed by TREF. In Figure 11 a comparison is made of branching distributions obtained for ethylene vinyl acetate (EVA) copolymers of 9, 14, and 18 wt % VA, as well as that for an ethylene–ethyl acrylate copolymer. As expected, increasing levels of VA show up as high levels of branching. It is interesting to note that the copolymer with ethyl acrylate is characterized by a broader, less smooth distribution compared to the corresponding EVA copolymer. This probably reflects the influence of differing reactivities of VA and EA with ethylene. It should be noted that these ethylene copolymers made by the high-pressure process also contain ethylene-type short-chain branching and that the data shown reflect the combined effects of this branching and that due to the comonomer. Whether the larger comonomer units disrupt crystallinity to different degrees than normal ethylene short-chain branching is not known at present although a study of this aspect is planned.

Throughout these series of fractionations the analytical TREF system worked well and was reasonably convenient to operate. The main experimental problem proved to be the difficulty in maintaining stable operation of the refractive index detector. Base-line drift, apparently due to room-temperature fluctuations and drafts, caused a number of runs to be aborted. Improved temperature stabilization of the detector housing and in particular of the preheat section, which conditions the eluent prior to flow through the detector block, should lead to improved operating efficiency. Under these conditions a schedule of two fractionations per day should be easily maintained. This is clearly a considerable improvement over the two to three runs a week experienced with the original preparative TREF system.

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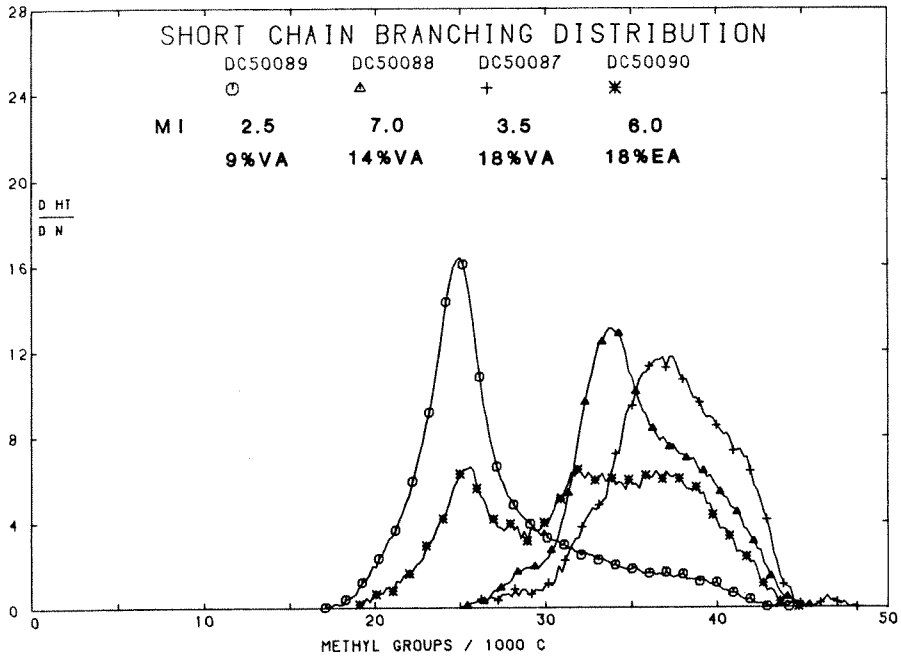


Fig. 11. SCB distributions obtained for ethylene copolymers: (⊙) MI 2.5, 9% VA; (▲) MI 7.0, 14% VA; (+) MI 3.5, 18% VA; (*) MI 6.0, 18% EA.

CONCLUSIONS

(i) Temperature-rising elution fractionation is an effective technique for fractionating polyethylenes with respect to degree of branching, as it is relatively free of molecular weight influences.

(ii) Use of smaller sample size and an on-line detector, as in the analytical TREF system described above, increases both the operating efficiency and the quality of the fractionation.

(iii) Calibration with suitable standards allows direct calculation of meaningful branching distributions. This elminates the need for analysis of individual fractions.

(iv) Analysis of a polyethylene resin using the TREF system in conjunction with size-exclusion chromatography provides a rapid evaluation of overall resin structure. This should provide a greater opportunity for elucidating the underlying reasons for the wide variations in behavior observed for polyethylenes and semicrystalline ethylene copolymers.

We wish to express our appreciation to Cornelia Key for her analysis of branching content, to Richard Bloss for the computer programming, and to Dr. R. Ranganath for his helpful discussions during the development of the new TREF technique.

References

1. F. M. Mirabella, Jr., and J. F. Johnson, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C12,** 81 (1975).
2. T. Ogawa, *J. Appl. Polym. Sci.*, **23,** 2315 (1979).
3. G. Riess and P. Callot, in *Fractionation of Synthetic Polymers*, L. H. Tung, Ed., Dekker, New York, 1977.
4. E. P. Otocka, R. J
5. L. Wild, R. Ranga
6. K. Shirayama, T.
7. K. Shirayama, S. I
8. V. Desreux and M
9. G. Allen, C. Booth
10. P. Kamath and L.
11. P. W. O. Wijga, J.
12. A. Nakajima and I
13. C. Bergström and
14. A. J. Pennings, *J.*
15. P. J. Flory, *Trans.*

Received April 6, 19
Accepted August 18

4. E. P. Otocka, R. J. Roe, M. Y. Hellman, and P. M. Muglia, *Macromolecules*, **4,** 507 (1971).
5. L. Wild, R. Ranganath, and T. Ryle, *J. Polym. Sci. A-2*, **9,** 2137 (1971).
6. K. Shirayama, T. Okada, and S. Kita, *J. Polym. Sci. A-2*, **3,** 907 (1965).
7. K. Shirayama, S. Kita, and H. Watabe, *Makromol. Chem.*, **151,** 97 (1972).
8. V. Desreux and M. C. Spiegels, *Bull. Soc. Chim. Belg.*, **59,** 476 (1950).
9. G. Allen, C. Booth, and M. N. Jones, *Polymer*, **5,** 257 (1964).
10. P. Kamath and L. Wild, *Polym. Eng. Sci.*, **6,** 213 (1966).
11. P. W. O. Wijga, J. van Schooten, and J. Boerma, *Makromol. Chem.*, **36,** 115 (1960).
12. A. Nakajima and H. Fujiwara, *Bull. Chem. Soc. Jpn*, **37,** 909 (1964).
13. C. Bergström and E. Avela, *J. Appl. Polym. Sci.*, **23,** 163 (1979).
14. A. J. Pennings, *J. Polym. Sci., C*, **16,** 1799 (1967).
15. P. J. Flory, *Trans. Faraday Soc.*, **51,** 848 (1955).

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EXHIBIT B

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.

REFERENCES

1. V. Desreux, M.C. Speigels, Bull. Soc. Chem. Belges, 59, 476, (1950).

2. C. Bergstrom, E. Avela, Kemia-Kemi Helsinki, 3, 47, (1976).

3. K. Shirayama, T. Okada, S. Kita, J. Poly. Sci., A. 3, 907, (1965).

4. L. Wild, T. Ryle, Polymer Reprints, 18, (2), 182, (1977).

5. L. Wild, T.R. Ryle, D.C. Knobeloch, I.R. Peat, J. Polym. Sci., Polym. Phys. Ed., 20, 441, (1982).

6. L. Wild, T. Ryle, D. Knobeloch, Polymer Preprints, 23, (2), (1982).

7. C. Bergstrom, E. Avela, J. Appl. Polym. Sci., 23, 163, (1979).

8. C. Elston, U.S. Patent 3,645,992, (1972).

9. P. Flory, Principles of Polymer Chemistry, (10th Printing), Cornell University Press, p. 568, (1978).

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.

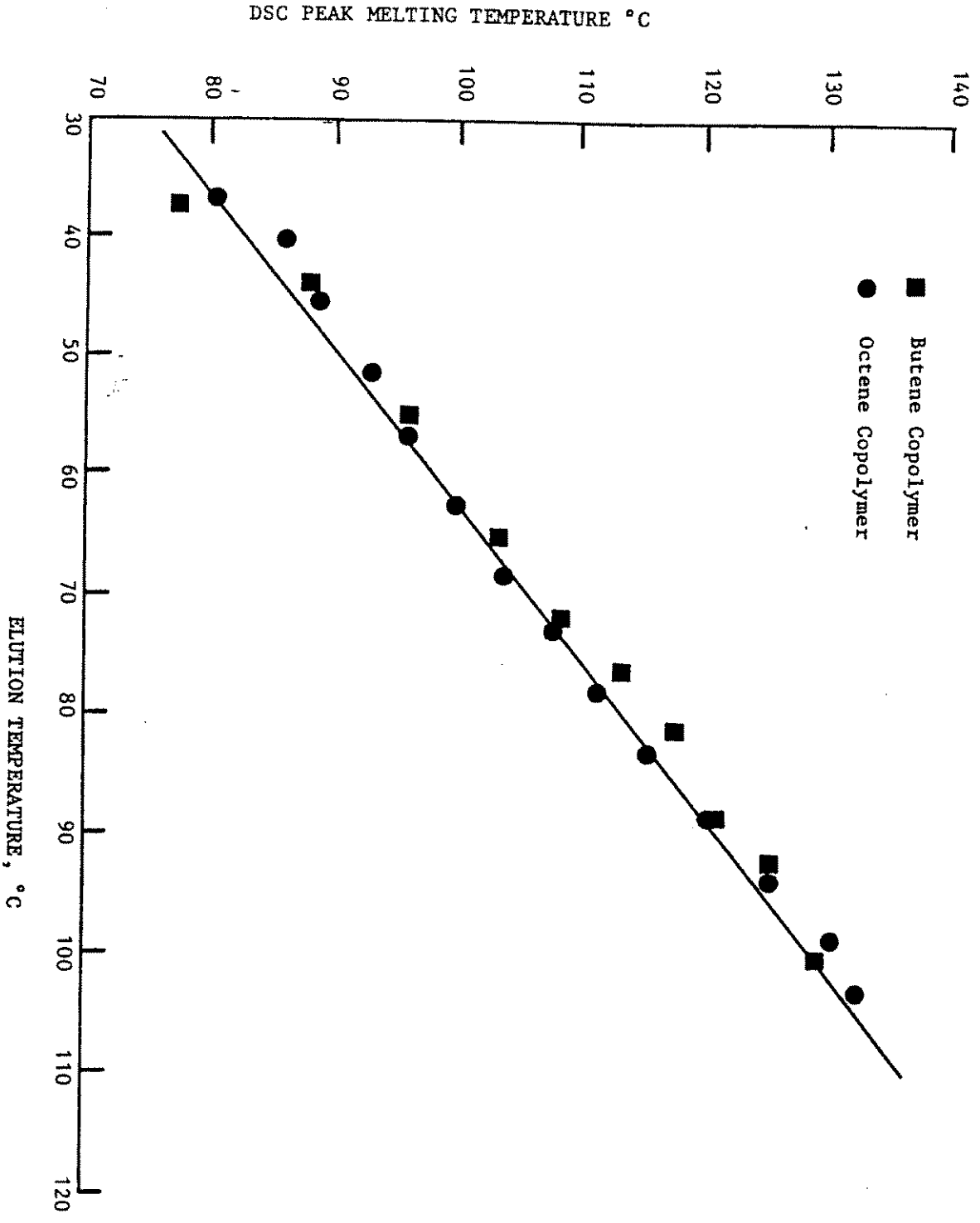
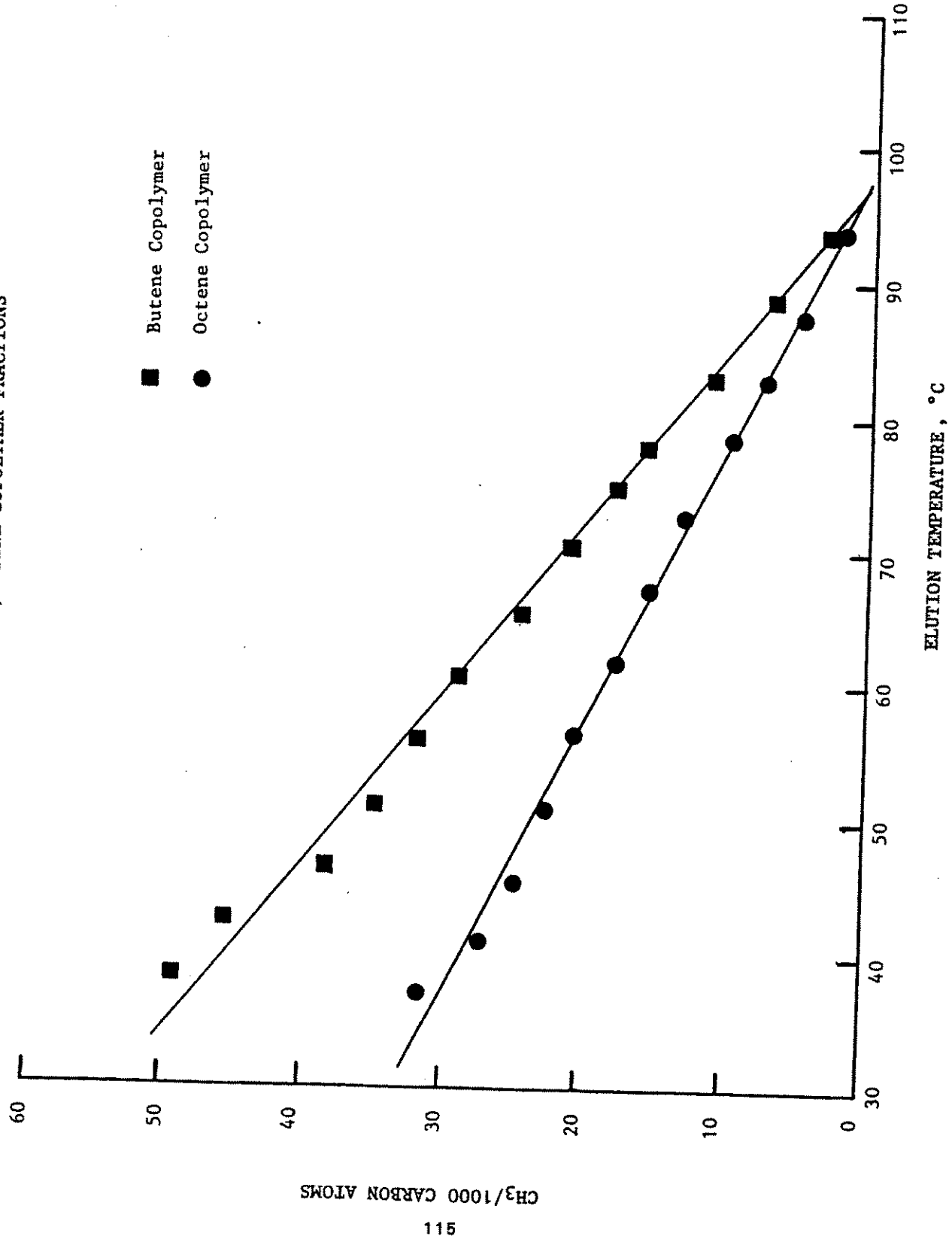


FIGURE 1
MELTING POINT VS. ELUTION TEMPERATURE FOR ETHYLENE/BUTENE AND ETHYLENE/OCTENE COPOLYMER FRACTIONS

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



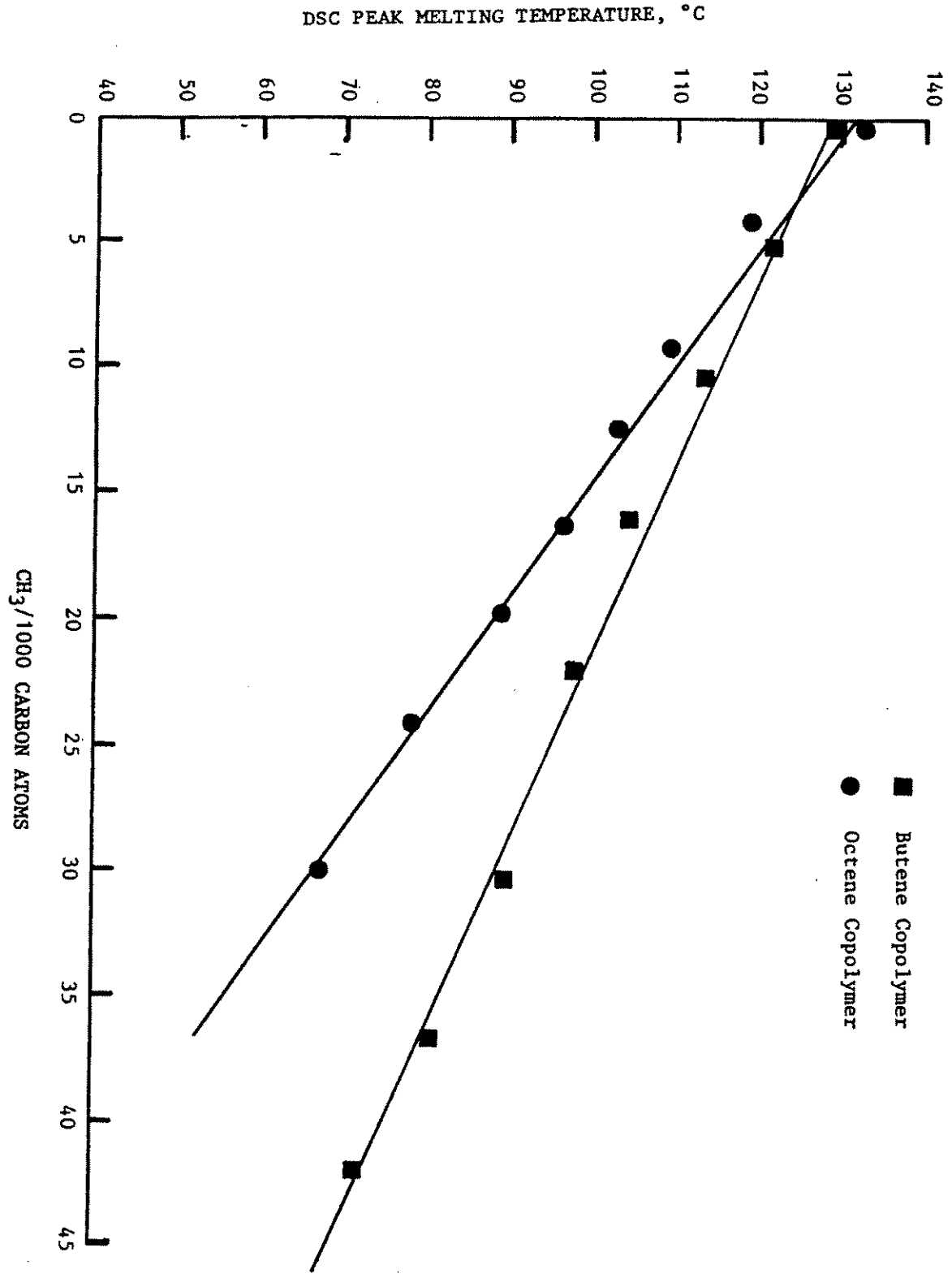


FIGURE 3
DSC MELTING POINT VS. DEGREE OF SHORT CHAIN BRANCHING FOR ETHYLENE/BUTENE AND ETHYLENE/OCTENE COPOLYMER FRACTIONS

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

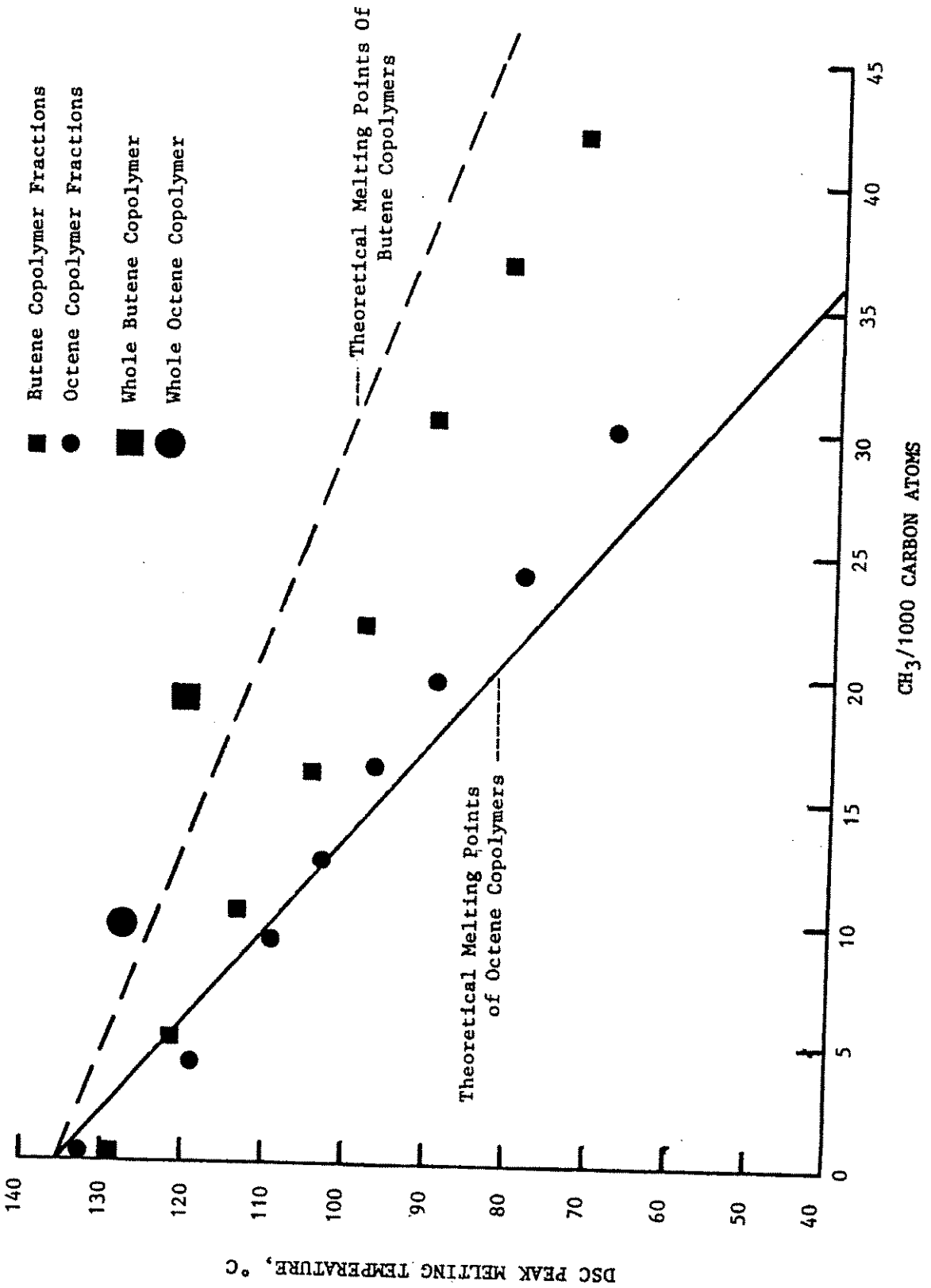


FIGURE 5

SCBD OF LLDPE-A ETHYLENE/BUTENE COPOLYMER

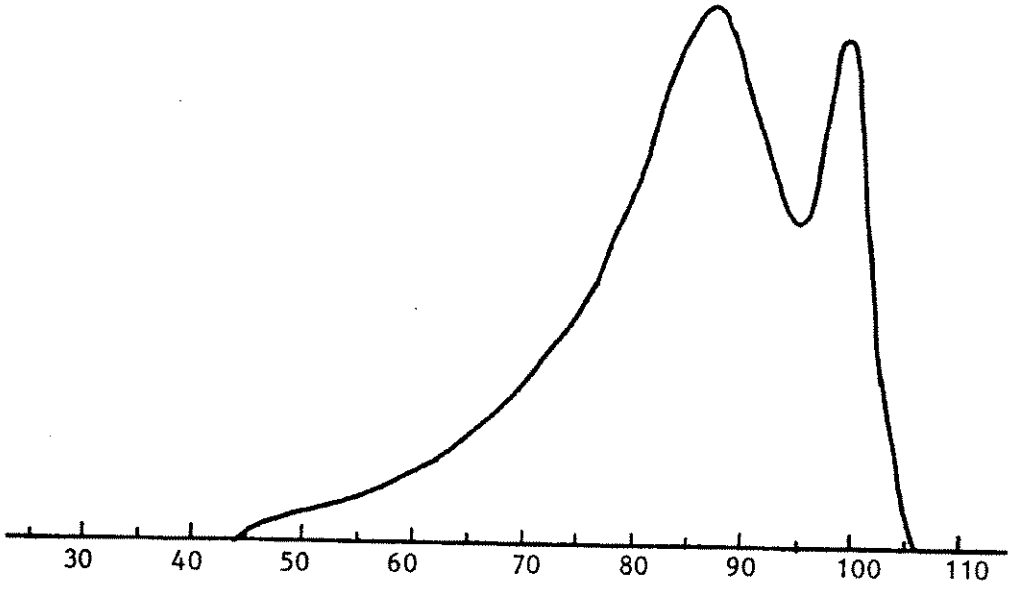


FIGURE 6

SCBD OF LLDPE-B ETHYLENE/HEXENE COPOLYMER

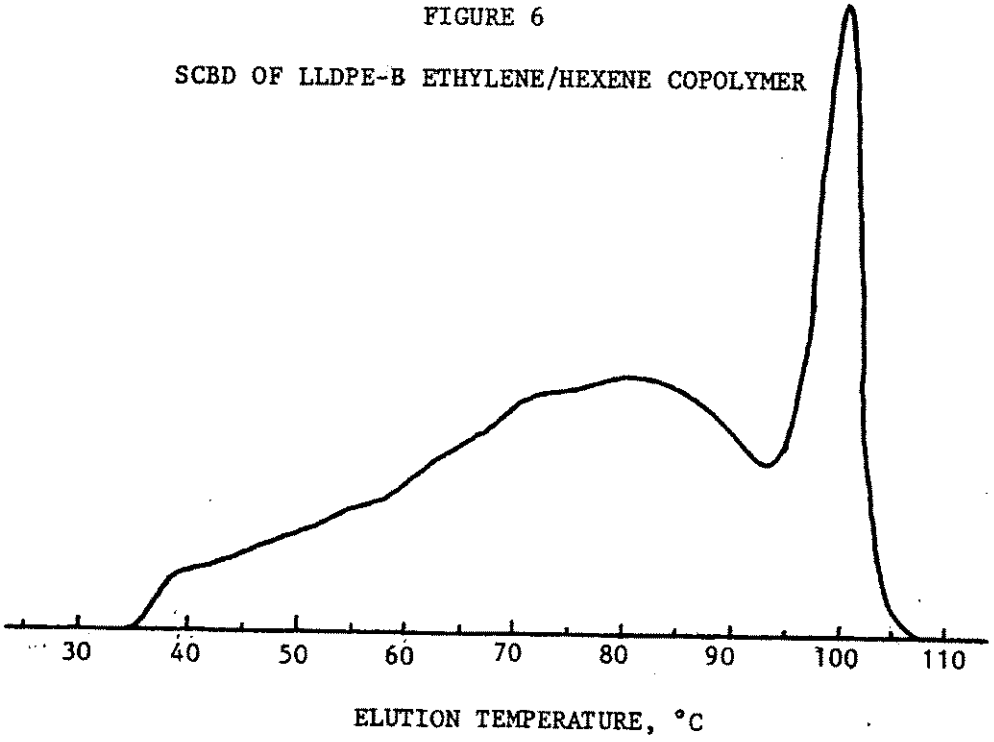


FIGURE 7

SCBD OF LLDPE-C ETHYLENE/OCTENE COPOLYMER

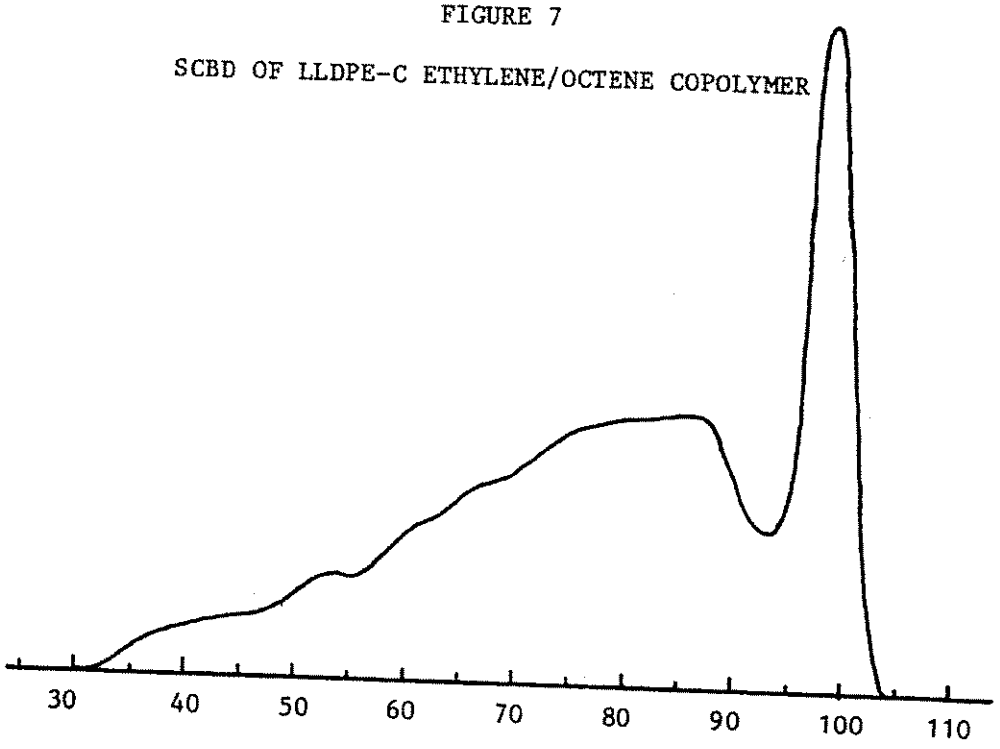
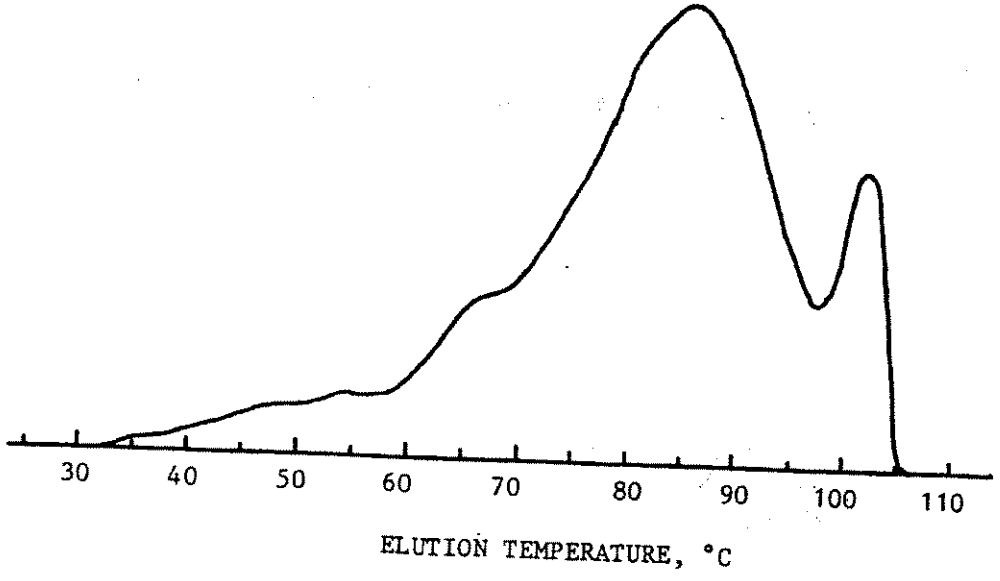


FIGURE 8

SCBD OF LLDPE-D ETHYLENE/OCTENE COPOLYMER



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