

# Investigation of the Composite Molecular Structure of LDPE by Using Temperature Rising Elution Fractionation

CHRISTER BERGSTRÖM, *Pekema Oy, SF-06850 Kulloo, Finland*, and  
EERO AVELA, \* *Department of Polymer Technology, Åbo Akademi,  
Porthansgatan 3-5, SF-20500 Åbo 50, Finland*

## Synopsis

In the synthesis of low-density polyethylene there is a direct relationship between the synthesis conditions, molecular structure, and technical properties of the product. The evaluation of the molecular structure of the polymer is therefore important. The most important structure parameters in low-density polyethylene are molecular weight distribution (MWD), degree of long-chain branching (LCB), and short-chain branching distribution (SCBD). Through chain transfer to polymer it is possible to get composite molecules made up of chains with different amounts of short-chain branching. By using temperature rising elution fractionation (TREF) and plotting the methyl contents or the DTA melt temperatures of the fractions as functions of the elution temperature, the SCBD within composite molecules can be evaluated. The deviations from linear relationships are caused by such SCBD within composite molecules. In order to demonstrate the buildup of composite molecules, samples from different parts of a reactor were investigated.

## EVALUATION OF SHORT-CHAIN BRANCHING DISTRIBUTION (SCBD) IN LDPE

Analytical and physical methods can be used to investigate the degree of short-chain branching (SCB) in LDPE. SCB increases the amount of methyl groups in the polymer, and these can be analyzed with an IR spectrophotometer. The crystalline structure in LDPE is disrupted by SCB, and this enables physical methods to be used for measuring the amount and distribution of SCB. Early investigations of SCBD in LDPE were made by using temperature rising elution fractionation (TREF) and measuring the methyl contents of the fractions. The weight distribution of different methyl contents was taken as a measure of SCBD.<sup>1,2</sup>

Temperature rising elution fractionation can be performed continuously using the fractionator seen in Figure 1.<sup>2</sup> The 5-liter column is filled with Chromosorb and loaded with a 4-g polymer sample as a 1% xylene solution. The temperature of the column is 120°C when loaded. Then, the column is cooled down quite quickly to 90°C and after that, a cooling rate of 1°C/hr is used until 40°C is reached. This slow cooling rate is necessary in order to achieve complete crystallization and good separation when fractionating. Elution with xylene (20 ml/min) is made while the temperature is raised (4°C/hr) from 50° to 90°C; every hour, four fractions are collected. The polymer in the fractions is precipitated with ethanol and filtrated. After drying the polymer is weighed.

\* Present address: Technical Research Centre of Finland, Chemical Laboratory, SF-02150 Espoo 15, Finland.

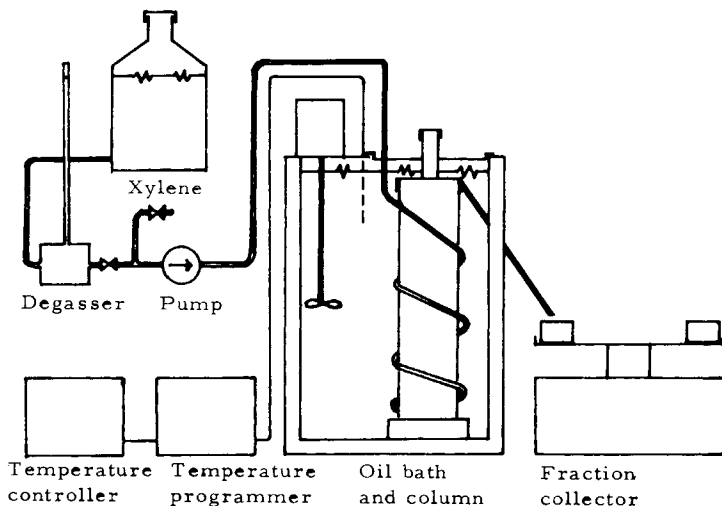


Fig. 1. Temperature rising elution fractionator.

The methyl content of LDPE can be measured according to ASTM D 2238-64T (Method B) or ASTM D 2238-68 (Methods A and B). In both cases the IR analyses are made from pressed plaques, and the methyl absorption at  $\lambda = 7.25 \mu\text{m}$  is measured. By the former method the ratio of the absorbances  $-\text{CH}_3/-\text{CH}_2-$  gives  $\text{CH}_3/1000\text{C}$  from a calibration curve, and by the latter method the  $-\text{CH}_2-$  absorbance peak is eliminated by using in the reference beam, a wedge made of polyethylene with a low and known  $\text{CH}_3$  content. It is necessary to use the latter method when copolymers of ethylene and isobutylene or propylene are investigated.

When polyethylene is allowed to crystallize very well, DSC or DTA analyses give curves which have widths that are proportional to the SCBDs. This can be done by crystallizing in a 1% xylene solution from  $80^\circ$  to  $30^\circ\text{C}$  with a cooling rate of  $1^\circ\text{C}/\text{hr}$  and analyzing a 5-g sample using a heating rate of  $5^\circ\text{C}/\text{min}$ .<sup>2</sup>

Evaluation of SCBD can also be made by plotting the normalized weights of the TREF fractions as a function of elution temperature or methyl content. These methods give roughly the same results and they are similar to the DSC or DTA curves made after a slow crystallization from the xylene solution.<sup>2</sup>

The differences in results of the methods described above merit further investigation in any event. Especially the methyl content of the TREF fractions do not correlate very well with the elution temperatures of TREF or the oven temperatures of DSC or DTA.<sup>2</sup>

### COMPOSITE MOLECULAR STRUCTURES OF LDPE AND THEIR INVESTIGATION WITH TEMPERATURE RISING ELUTION FRACTIONATION (TREF)

Increasing temperature and decreasing pressure in the reactor increase the amount of SCB in LDPE. Also the amount of LCB increases, especially at high conversion and mixing efficiencies.<sup>3</sup> By using different temperatures in different parts of the reactor, the branches developing after the chain transfer to polymer may have different amounts of SCB than the rest of the molecule (a composite molecule).

In an autoclave reactor with the synthesis gas fed from the top and the LDPE product taken out from the bottom the following grades were made and investigated.

Grade 1 was synthesized with the same temperature ( $T$ ) in all parts of the reactor, and the conversion in the upper half of the reactor was about 70% of the total. The product had a melt index of 3.1 and a density of 0.924. A GPC analysis<sup>4</sup> gave a  $\overline{M}_w/\overline{M}_n$  of 11.1 and a long-chain branching index ( $\lambda$ ) of  $0.82 \times 10^{-4}$ .

Grade 2 was synthesized under the same reactor conditions as grade 1, except for the temperature in the lower half of the reactor, which was  $45^\circ\text{C}$  higher ( $T + 45^\circ\text{C}$ ). In this way composite molecules were formed. The product had a melt index of 3.2 and a density of 0.921. A GPC analysis<sup>4</sup> gave a  $\overline{M}_w/\overline{M}_n$  of 16.3 and a long-chain branching index ( $\lambda$ ) of  $1.1 \times 10^{-4}$ .

Grade 3 was synthesized at temperature  $T - 55^\circ\text{C}$  in the top of the reactor and  $T + 50^\circ\text{C}$  at the reactor outlet with the temperature rising continuously in the lower half of the reactor. The conversion in the upper half of the reactor was about 70% of the total. The reactor pressure was much lower than for grades 1 and 2, and in the top of the reactor there were two-phase conditions, which means that at quite low reactor temperatures and pressures all the polymer does not dissolve in ethylene but the big molecules form a separate polymer-rich phase.<sup>5-10</sup> The product had a melt index of 0.71 and a density of 0.921. A GPC analysis<sup>4</sup> gave a  $\overline{M}_w/\overline{M}_n$  of 2.1 and a long-chain branching index ( $\lambda$ ) of  $0.64 \times 10^{-4}$ .

A linear polyethylene synthesized with 1-butylene as comonomer was fractionated as a reference. The product had a melt index of 0.24 and a density of 0.925. A GPC analysis<sup>4</sup> gave a  $\overline{M}_w/\overline{M}_n$  of 5.25.

The polymer grades described above have in principle molecular structures as seen in Figure 2.

In order to investigate the effect of composite molecular structure on temperature rising elution fractionation, the fractions were analyzed with an IR spectrophotometer and DTA. The methyl contents (Fig. 3) and the DTA melt temperatures (the temperatures at the half-height obtained by halving the distance between the baseline and the DTA peak) (Fig. 4) were then plotted as functions of the TREF elution temperature.

As seen from Figure 3, only the reference has a linear correlation between the methyl content and the TREF elution temperature. All the other grades have higher methyl contents in the later fractions, and grade 3 even in the earlier fractions. One might think that composite molecules are dissolved in the TREF column only when the chains containing least SCB are dissolved, but the methyl contents measured with an IR spectrophotometer are average values of all the chains in the fractions. Grade 1 probably also has composite molecules to some

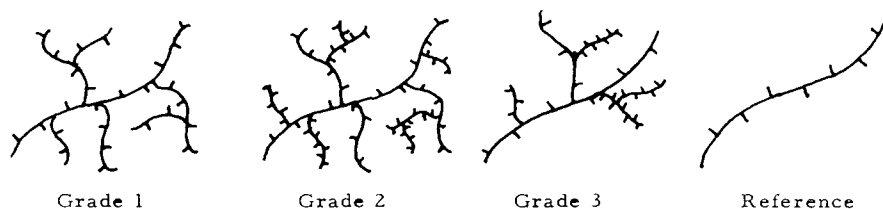


Fig. 2. Molecular structures of LDPE grades studied.

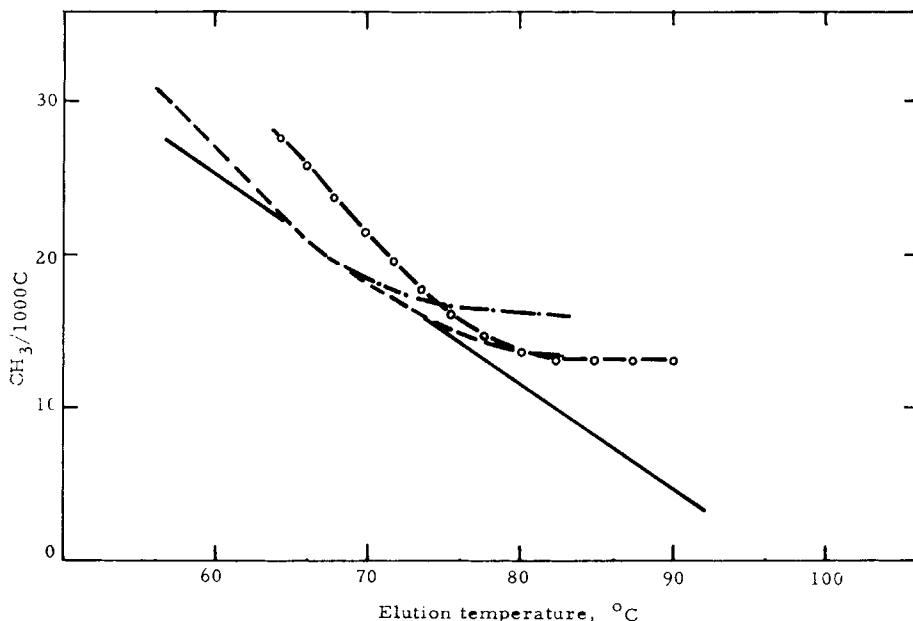


Fig. 3. Methyl content of TREF fractions: (---) grade 1; (-·-) grade 2; (-○-) grade 3; (—) reference.

extent because the polymer is synthesized to quite a high conversion, and this causes temperature gradients in the reactor. But when the reactor bottom temperature is increased by 45°C, the methyl contents of the later fractions rise significantly. In grade 3 the methyl contents do not rise that much because the reactor bottom temperature increases only gradually, and at least part of the polymer-rich droplets synthesized in the top of the reactor do not dissolve in the bottom of the reactor and are therefore prevented from forming composite molecules.

Figure 4 reveals that the melting range is broader for the fractions containing composite molecules (grades 2 and 3) as compared to the fractions of grade 1 and the reference. The absolute melt temperatures, on the other hand, differ considerably depending on the grade fractionated.

#### INVESTIGATION OF SAMPLES TAKEN FROM DIFFERENT PARTS OF A STIRRED LDPE REACTOR

In order to study the buildup of composite molecules and their influence on the TREF results, the reaction was stopped after synthesizing grade 3, the stirrer was taken out of the reactor, and the polymer sticking to the stirrer shaft was investigated. Samples A, B, C, D, and E (the final product) were taken as seen in Figure 5.

The stirrer samples were yellowish because of oxidation, and only about 30% of each sample was dissolved in hot xylene. The dissolved and the nondissolved parts of the samples were investigated separately. The methyl contents of the polymer samples were measured with an IR spectrophotometer, and DTA analyses were made after cooling slowly in xylene. The dissolved parts of the samples were also analyzed with GPC,<sup>4</sup> and the weight-average molecular weights of the samples were compared.

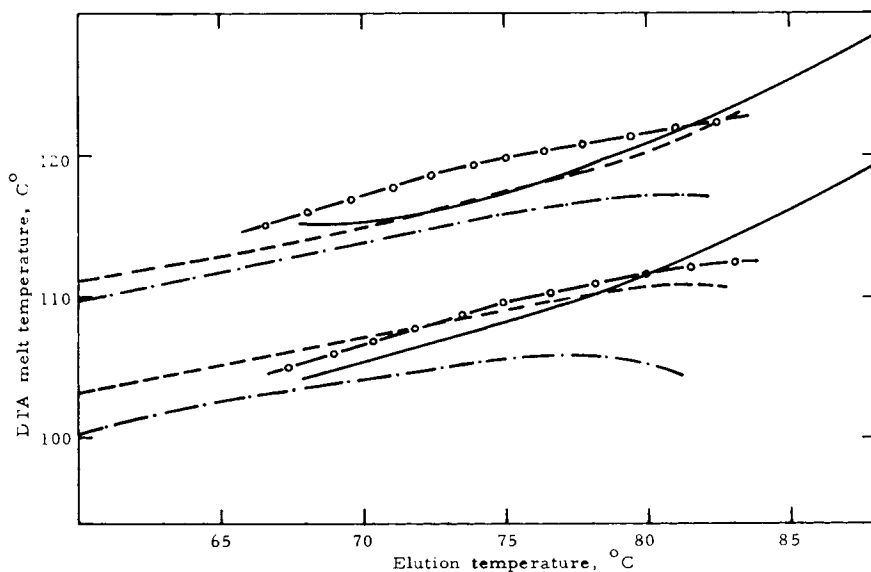


Fig. 4. DTA melt temperatures of TREF fractions: (---) grade 1; (- · -) grade 2; (- O -) grade 3; (—) reference.

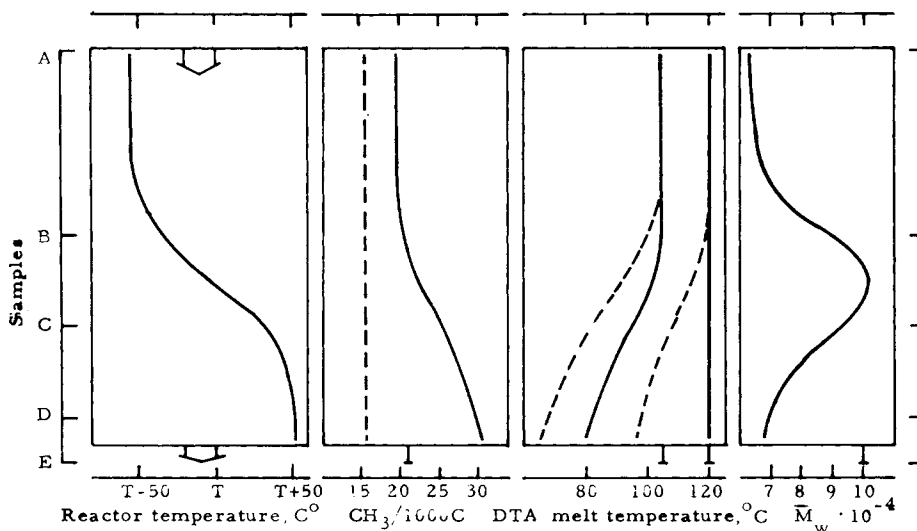


Fig. 5. Properties of low-density polyethylene deposited at different levels in an autoclave reactor: (—) polymer dissolved; (---) polymer not dissolved.

The dissolved parts of the samples were fractionated with TREF (sample weights 0.5 g), and the fraction weight distributions were plotted as a function of elution temperature (Fig. 6). The methyl contents are plotted in Figure 7, and in Figure 8 the DTA melt temperatures (half-height temperatures) are shown as functions of the TREF elution temperature.

In Figure 5 we see that the polymer dissolved acquires a higher methyl content when the reactor temperature is rising. The nondissolvable polymer, on the other hand, has the same methyl content in all parts of the reactor. The product has a methyl content about the same as the dissolved sample from the top of the reactor. This is also the case when looking at the DTA half-height temperatures.

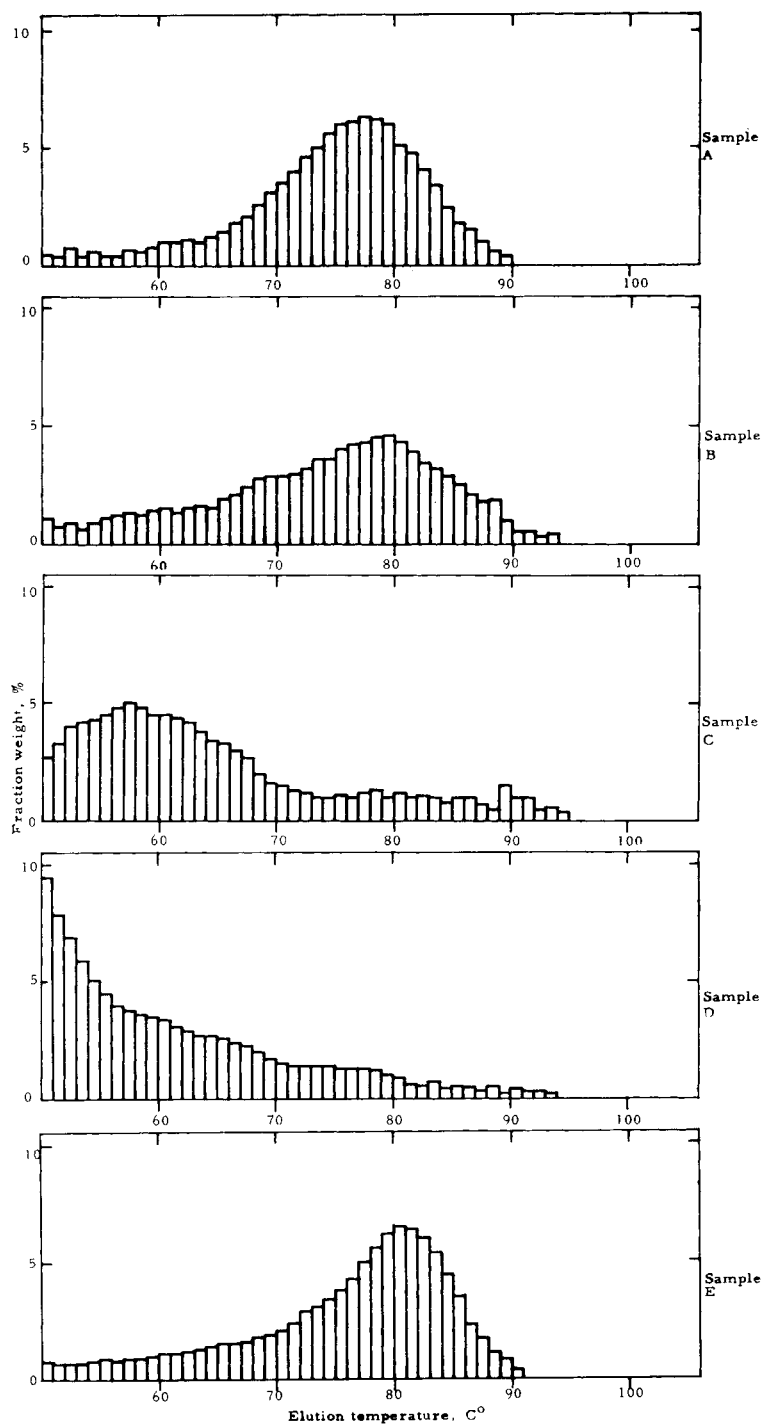


Fig. 6. Distribution of TREF fractions as a function of elution temperature for samples A, B, C, D, and E.

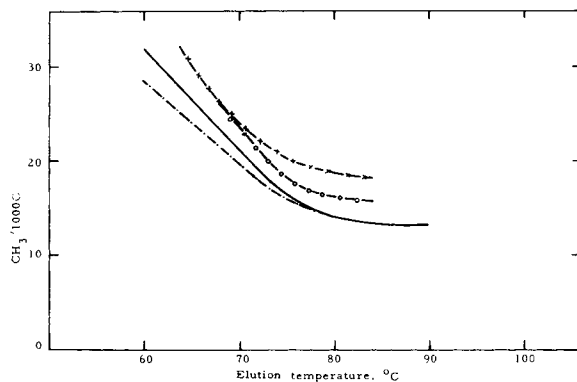


Fig. 7. Methyl content of TREF fractions: (---) samples A and B; (-x-) sample C; (-o-) sample D; (—) sample E.

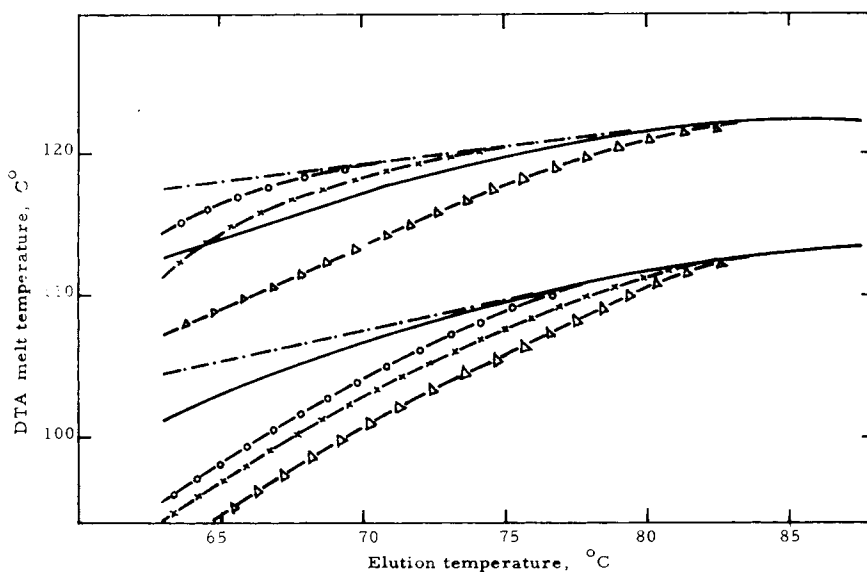


Fig. 8. DTA melt temperatures of TREF fractions: (-·-) sample A; (-Δ-) sample B; (-x-) sample C; (-o-) sample D; (—) sample E.

In the bottom of the reactor one finds polymer which starts to melt quite early, but the higher half-height temperature is the same as that for the product and the polymer in the top of the reactor. The same highly crystalline polymer is found in every place, and the less crystalline polymer is partly grafted to it and exists partly as separate molecules. The polymer not dissolved melts at the same temperature as the dissolved polymer in the top of the reactor, but in the bottom of the reactor both DTA half-height temperatures are lower for the polymer not dissolved, even if its methyl content is the same all through the reactor. This low degree of crystallinity might be due to more crosslinking. It might be that the polymer-rich droplets developed in the two-phase conditions in the top of the reactor are for some reason more sensitive to crosslinking and to a high degree affect the properties of the polymer not dissolved. These droplets are not completely dissolved in ethylene in the bottom of the reactor as seen from the constant methyl content. The reason for the difference between the DTA

half-height temperatures of the product again being quite small might be that there is an excessively low portion of less crystalline polymer to be seen by DTA.

From the  $\bar{M}_w$  values we see that the molecular weights of the stirrer samples dissolved are low compared to that of the product. This fact proves that the big molecules do not dissolve and under two-phase conditions are concentrated in the polymer-rich droplets. In the middle of the reactor the  $\bar{M}_w$  values increase because some of the high molecular weight droplets dissolve as the temperature rises. In the bottom of the reactor the  $\bar{M}_w$  values decrease again under the influence of the high synthesis temperature.

When comparing the distributions of TREF fractions on the basis of elution temperature (Fig. 6), we see that we get more of the less crystalline material from samples synthesized at a higher temperature closer to the bottom of the reactor. The product has more highly crystalline material than the stirrer samples, and this is probably because the highly crystalline molecules are also big and therefore concentrated in the two-phase droplets.

Figures 7 and 8 contain the methyl contents and the DTA half-height temperatures of the TREF fractions. We see that the product is about the same as the samples from the top of the reactor. Only the earlier fractions have higher methyl contents and lower DTA half-height temperatures probably because of grafting in the bottom of the reactor. When looking at the lower DTA half-height temperatures, we have the lowest values for sample B, and then these temperatures rise as one approaches the bottom of the reactor. This might be so because when approaching the bottom the proportion of grafted less crystalline material decreases as the two phase droplets dissolve. The methyl contents indicate just the same for the two bottom samples, but the methyl contents of the fractions from sample B are the same as for the sample from the top of the reactor.

## DISCUSSION

The results presented above provide us with a tool for evaluating the structure of composite LDPE molecules. By plotting the weight distribution of TREF fractions, their methyl contents, and DTA half-height temperatures as functions of elution temperature, information of the short-chain branching distribution between the fractions as well as within the fractions is obtained. The effect of composite molecules on these results was systematically investigated by using samples taken from different parts of the reactor, and the results could easily be explained. When, on the other hand, LDPE grades synthesized under very different synthesis conditions are compared, the results no longer reflect differences in the composite molecules so accurately, but even in this case the investigation methods used in this work can improve our understanding of LDPE synthesis and its effect on molecular structure.

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Received July 8, 1977

Revised October 14, 1977