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## Gel permeation chromatography–Fourier transform infrared study of some synthetic polymers

### II. Instrumentation for the characterization of polyethylene<sup>a</sup>

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#### ABSTRACT

A high-temperature gel permeation chromatography–Fourier transform infrared (GPC–FT-IR) system was developed to characterize commercially available polyethylene. High-temperature transfer tubing was used to connect the high-temperature flow cell of an FT-IR spectrophotometer and a high-temperature GPC system. The GPC–FT-IR system was calibrated to determine the molecular weight distribution (MWD) and the short-chain branching (SCB) for high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE). The MWD and SCB of a commercial LLDPE determined using the present GPC–FT-IR system compared favourably with those measured with a solvent gradient elution fractionation technique where <sup>13</sup>C NMR spectrometry was employed to determine the SCB for the same PE.

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#### INTRODUCTION

Gel permeation chromatography (GPC) has often been used to characterize synthetic polymers. GPC separates molecules according to size difference. The molecular weight distribution (MWD) obtained from GPC is often used to characterize synthetic polymers. In the polymer industry, GPC is commonly used to inspect

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<sup>a</sup> For Part I, see ref. 1.

the molecular weights (MW) and the MWD of polymers for quality control purpose<sup>2,3</sup>.

Whereas molecular weights and distributions are convenient parameters to correlate with the physical properties of polymers, such as mechanical strength and stress cracking resistance, other properties such as branching, formation of multiple bonds and inversion of head-to-tail sequences also influence not only the chemical properties but also the physical properties of synthetic polymers<sup>4</sup>. Therefore, spectroscopic methods such as infrared (IR)<sup>5</sup> and nuclear magnetic resonance (NMR)<sup>6</sup> have been widely adopted as alternative methods for characterizing bulk synthetic polymers.

When an IR spectrometer is connected to a GPC system as a detector, it is possible to obtain spectroscopic information regarding the chemical composition of the polymer fraction in each elution volume instantly. Using a dispersive IR spectrometer as a GPC detector in a stop-and-go mode, Mirabella and Barrall were able to determine the chemical composition distribution of some copolymers as a function of MW. Their study showed that there is a drift of the chemical composition with respect to molecular weight, although the information obtained by their method is rather primitive compared with that obtained by complete chemical composition analysis. However, information obtained by GPC-IR still provides valuable data on chemical composition as a function of MW for certain polymer manufacturers. A Fourier transform IR (FT-IR) system is the most suitable detector for such studies, as it is capable of obtaining a full-range (4000–700  $\text{cm}^{-1}$ ) IR spectrum within 1 s without stopping the flow.

Recently, linear low-density polyethylene (LLDPE) has become commercially important, and the distribution of the short-chain branching (SCB) of LLDPE has been found to be heterogeneous. It is claimed in a recent patent application<sup>8</sup> that the distribution of SCB in the case of high-density polyethylene (HDPE), exhibiting a heterogeneous chemical composition, is related to the physical properties of PE such as resistance to stress cracking.

We wished to develop a GPC-FT-IR system to determine the SCB as a function of MW for commercial HDPE and LLDPE. In this paper, the details of such a GPC-FT-IR system are described, in which GPC is used to separate HDPE and LLDPE on the basis of molecular size and an FT-IR spectrophotometer is used to obtain information on the chemical structure during the GPC analysis. Several kinds of PE were included in this study.

## EXPERIMENTAL

### *Instrumentation*

A Perkin-Elmer Model 1700 FT-IR spectrometer, equipped with a narrow-band mercury-cadmium-telluride (MCT) cold detector, and a Model 7700 computer with CDS-3 software for post-run data handling and interfacing to the GPC system, was used as a detector in combination with a Waters Assoc. Model 150C high-temperature gel permeation chromatograph. A 60-cm TSK-GMH4 column (Toyo Soda) with 1,2,4-trichlorobenzene (TCB) or *o*-dichlorobenzene (ODCB) as solvent was used for polymer separation. These solvents do not show strong absorption of infrared light in the range 3000–2700  $\text{cm}^{-1}$  (see below).

The GPC system, including autosampler, injector, column and refractive index (RI) detector, was operated at 135°C. The column eluate was directed to a heated flow cell (quartz windows, 1 mm optical path length, *ca.* 30  $\mu$ l cell volume). A GPC curve typically appears *ca.* 10–15 min after injection of 1 ml of PE solution. A series of IR spectra were measured and accumulated for 15 s (seventeen scans) and each piece of accumulated data was stored as one file of time-sliced GPC data. Usually *ca.* 30 files were stored for one run, including a few files before and after the peak. It was necessary to inject 1 ml of solution to obtain a strong IR signal, although the usual GPC analysis requires the injection of smaller sample volumes.

In order to ensure that the GPC pattern is free from distortion due to the diffusion in the flow cell and overloading of the sample, the flow was returned to the built-in RI detector through a two-way heated transfer tube. The temperatures of both the flow cell and the transfer tubing were maintained at 135°C.

MWD, were calculated from GPC curves obtained with the RI and IR detectors using a universal calibration method which uses polystyrene standards<sup>9</sup>. In this study, the GPC curve constructed from the IR spectra, *i.e.*, the peak area of the C–H stretching vibration appearing in the range 3000–2700  $\text{cm}^{-1}$ , was plotted against the MW of the PE fraction for each retention volume, assuming that the Lambert–Beer law holds in this region.

All the stored spectra were automatically processed by the system computer to generate a report.

#### *Measurement of GPC-FT-IR spectra*

Commercial samples of LLDPE, HDPE and high-pressure, low-density polyethylene (HP-LDPE) dissolved in TCB at a concentration of 3 mg/ml at 135°C were used. A single-beam IR spectrum was observed before PE was eluted from the column as a background spectrum and each time-sliced single-beam spectrum of the eluate was divided by this background spectrum to give the PE spectrum in the range 3000–2700  $\text{cm}^{-1}$ . All of the IR spectra were measured at 8  $\text{cm}^{-1}$  resolution. These time-sliced IR spectra were used to calculate the number of methyl groups per 1000 carbon atoms based on the intensity ratio between methyl and methylene groups at 2965 and 2928  $\text{cm}^{-1}$ , respectively.

#### *Fractionation and cross-fractionation of PE*

Solvent gradient elution fractionation (SGEF) of 5 g of a commercial LLDPE-A (1-octene as co-monomer) was carried out using a column filled with 250 g of Celite (Johns Manville)<sup>10,11</sup>. Eight fractions were collected and each fraction was characterized by <sup>13</sup>C NMR and GPC methods. The detailed procedure for the SGEF–NMR method was described in Part I<sup>1</sup>.

Fractionation of LLDPE-A was performed by the temperature-rising elution fractionation (TREF) technique to cross-fractionate the resin by crystallinity<sup>12</sup>. The two-step technique involves the deposition of LLDPE from xylene solution at 140°C on inert glass beads by gradually cooling the solution, so that the glass beads will be coated by fractions with poor solubility to xylene as the inner layers and gradually by fractions with higher solubility in the outer layers. When all of the resin had been precipitated on the glass beads, the coated polymer layer was extracted with xylene. The extraction was carried out by increasing the temperature slowly from ambient to

130°C. A 5-g amount of LLDPE gave twelve fractions. The MWD of the PE resin in each fraction was measured with the GPC system.

In order to obtain information of the number of methyl groups per 1000 carbon atoms at different MWs, each TREF eluate of LLDPE-A was fed to the GPC system and several fractions were collected from each GPC run. PE was drawn from solvent to prepare a PE film and the number of methyl groups was determined using the  $1381\text{ cm}^{-1}$  peak intensity due to methyl groups, and their MWs were calculated from the GPC data. The experimental procedure and the three-dimensional display of the data from TREF technique have been described elsewhere<sup>13,14</sup>.

## RESULTS AND DISCUSSION

### *Determination of SCB as a function of MWD by the GPC-FT-IR method as compared with the SGEF-NMR method*

The SCB of LLDPE is intentionally introduced by the addition of certain olefin monomers such as 1-butene, 1-hexene, 1-octene or 4-methyl-1-pentene. For example, 1-butene introduces an ethyl side-chain into PE molecules. Hence both the methyl group in this short chain and the terminal methyl group give rise to a C-H stretching vibration in the IR spectrum. As the absorptions of methyl and methylene C-H stretching vibrations appear at  $2965$  and  $2928\text{ cm}^{-1}$ , respectively, the ratio of the number of methyl to methylene groups will be given by the intensity ratio of  $\text{CH}_3$  and  $\text{CH}_2$  absorptions,  $A^{2965}(\text{CH}_3)/A^{2928}(\text{CH}_2)$ . As the signal intensity of the methyl group is too weak to be recognized as a peak, the self-deconvolution technique<sup>15</sup> was adopted to reduce the line width and to separate the absorption of methyl groups from the intense absorption of methylene groups. The deconvoluted spectrum gives a sufficient signal intensity to be able to calculate the number of methyl groups.

In order to evaluate the branching of PEs, the numbers of methyl groups per 1000 carbon atoms,  $n/1000\text{C}$ , are calculated in the PE industry. A series of standard PE solutions were injected into the GPC system without a column and their IR spectra were measured to give  $A^{2965}$  and  $A^{2928}$  values for comparison of the  $n/1000\text{C}$  values.

These standards were obtained from 1-butene-modified LLDPE using the above-mentioned cross-fractionation method. We obtained a linear relationship between the number of methyl groups per 1000 carbons and the absorption ratio  $A^{2965}/A^{2928}$ . PE standards with similar MWs of *ca.* 100 000 were selected for this purpose in order to avoid any possible errors due to low- and high-molecular weight extremes.

As one of the two termini of the PE molecule is regarded as a methyl group and another as a vinyl group<sup>16</sup>, the degree of SCB was equal to the calculated amounts minus one. The number of terminal methyl groups per 1000 carbon atoms,  $n(t)/1000\text{C}$ , was therefore calculated with the equation

$$n(t)/1000\text{C} = 14\,000/M \quad (1)$$

where  $M$  is the molecular weight of PE in the eluate.

In addition, with LLDPE-A, one co-monomer molecule introduces an additional five  $\text{CH}_2$  groups, whereas an additional  $\text{CH}_2$  group was introduced for the 1-butene-modified LLDPE. Therefore, a proper correction should be made in order to

calculate the SCB accurately when the co-monomers of the standard and the sample LLDPE are different, as determination of the number of methyl groups depends not only the methyl group intensity but also on the methylene intensity. For instance, when 1-butene-modified LLDPE is used as a standard and 1-octene-modified LLDPE-A is analysed for SCB, the  $n/1000C$  value should be modified to take account of four extra methylene groups which lower the calculated number of methyl groups in 1-octene-modified LLDPE. With the assumption that the methylene groups in the side-chain and those in the molecular chain exhibit the same molar absorptivity, the contribution of an extra four in 1000 methylene groups (0.004) should be removed from the calibration equation. Therefore, the actual value of SCB,  $n/1000C(\text{act})$ , for 1-octene-modified LLDPE should be calculated from the observed value,  $n/1000C(\text{obs})$ , according to the equation

$$n/1000C(\text{act}) = n/1000C(\text{obs}) / \{1 - 0.004[n/1000C(\text{obs})]\} \quad (2)$$

Fig. 1 shows the SCB as a function of MW determined with the present GPC-FT-IR method (open circles) and with the SGEF-NMR method (solid circles). The results obtained with these two independent methods coincide completely<sup>a</sup>. This is also true even when there is a discontinuity in the MWD of SCB near the top of the peak in the GPC curve. The results indicate that the proposed GPC-FT-IR method can be regarded as more efficient than the SGEF method. Usually the SGEF technique takes 2-3 weeks to complete, whereas the present method takes only 1 h to achieve the same results.

#### *Characterization of LLDPE by GPC-FT-IR*

As indicated in the literatures, the TREF method fractionates the PE according to the SCB<sup>15</sup>, the SGEF method according to molecular weight<sup>16</sup> and the GPC method according to molecular size. As stated in the Introduction, the molecular size distribution can be approximated as the MWD, as shown in the previous section where the GPC-FT-IR method gave identical results with the SGEF-NMR method. In order to interpret the GPC-FT-IR data, we carried out the cross-fractionation of LLDPE-A by the TREF method and compared the data with those given by GPC-FT-IR.

Fig. 2 is a three-dimensional display of the relationship between the MW and SCB of LLDPE-A. Each of the twelve fractions given by the SGEF method was analysed by GPC for its MWD. Fig. 2 shows that the fraction with a small  $n/1000C$  value (1.4-2) has a narrow MWD and a higher average MW, whereas the MWD becomes wider and the average MW becomes smaller as the  $n/1000C$  value becomes larger. The average MW determined by GPC analysis of each fraction collected in the TREF method shown in Fig. 2 was plotted against the  $n/1000C$  value (Fig. 3). Fig. 3 indicates that the degree of SCB decreases as the MW of the resin increases, which

<sup>a</sup> The discrepancy of *ca.* one methyl group between the GPC-FT-IR and fractionation methods indicated in Part I<sup>1</sup> can be explained by the fact that *two* methyl groups were subtracted from the calculated values in the previous paper, instead of *one* methyl group as assumed in this paper. Also, the fourth line from the bottom of p. 527 in Part I<sup>1</sup> previous paper, should read, "the GPC-FT-IR method always gives one methyl *less* than the NMR method".

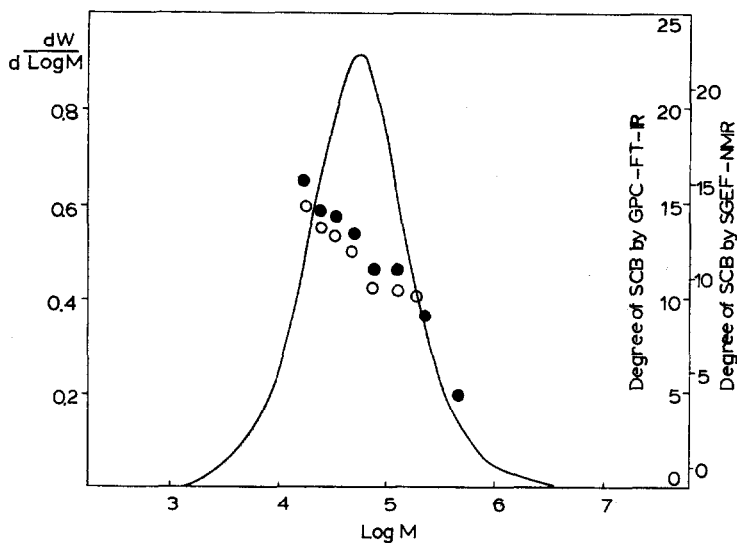


Fig. 1. Molecular weight distribution curve (solid line) detected by GPC-RI and molecular weight dependence of the degree of SCB per 1000 C as determined by (○) GPC-FT-IR and (●) SGEF-NMR methods.

illustrates a similar relationship between MW and  $n/1000C$  value to that in Fig. 1. The difference between Figs. 1 and 3 is not surprising, as the GPC-FT-IR method determines the degree of SCB for the narrow MW, whereas the TREF method determines the MWD of the PE fractions at a certain value of SCB.

#### *Application of GPC-FT-IR method to some LLDPE and HDPE*

As the present GPC-FT-IR method was found to give the same relationship between the SCB and MW as those determined from SGEF- $^{13}C$  NMR for the 1-octene-modified LLDPE-A, we carried out the characterization of some LLDPE and HDPE samples. Although the SCB of 1-butene-modified LLDPE (LLDPE-B) decreased monotonously from 20 to 8 methyl groups per 1000 carbons with increase in molecular weight, another kind of commercial LLDPE (LLDPE-C) showed an almost constant SCB of 9.5 methyl groups per 1000 carbons over the entire MW range. According to Hosoda<sup>16</sup>, LLDPE polymerized with  $TiCl_4$  and triethylaluminium supported on  $MgCl_2$  as catalysts shows a monotonous decreases in SCB with increase of MW, whereas the SCB of LLDPE, which is polymerized under homogeneous conditions with a soluble catalyst such as triethylaluminium sesquichloride and vanadium chloride, is almost independent of MW.

As HDPE is reported to have few branchings and, in addition, the branching is considered to be SCB<sup>17,18</sup>, attempts to utilize the present GPC-FT-IR method to characterize HDPE were carried out. First, we chose NBS SRM 1475 high density polyethylene (HDPE-A) for characterization. The SCB was indeed small (average 2.8 methyl groups per 1000 carbons) and was independent of MW.

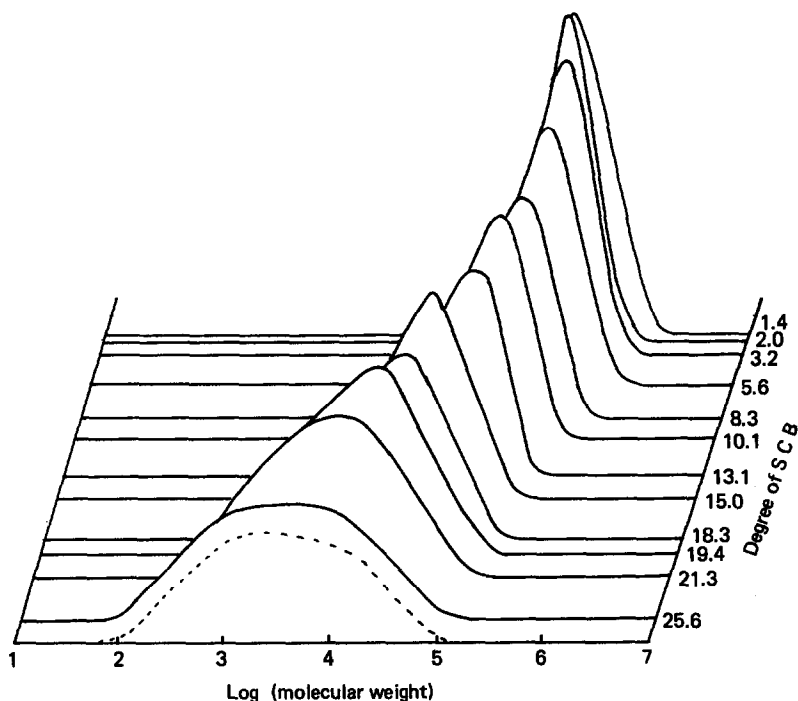


Fig. 2. Three-dimensional display of weight fractions ( $z$ -axis) cross-fractionated in terms of molecular weight ( $x$ -axis) and short-chain branching ( $y$ -axis).

Another material that we have characterized using the GPC-FT-IR method is a commercially available HDPE-B, which is used to make thin film for wrapping bags. Fig. 4 shows two peaks on the GPC curve, whereas the SCB is almost constant, with an average value of 5.2 methyl groups per 1000 carbons, over the entire MW range or increases slightly with an increase in MW. As it is abnormal to observe two peaks on the GPC curve of PE, the presence of two peaks suggests either that the material is a mixture of two different polymers or that two-step polymerization was carried out to manufacture the HDPE-B. The above-mentioned patent application<sup>8</sup> suggests the superiority of the physical properties of this HDPE-B from the fact that the SCB is independent of MW.

Finally we shall consider the results for HP-LDPE. As is well known, HP-LDPE has long-chain branching (LCB) in addition to SCB. As it is not possible to distinguish between LCB and SCB by IR spectroscopy, the number of methyl groups per 1000 carbon atoms was plotted against MW. It was demonstrated that the average value for HP-LDPE, *ca.* 26.9 methyl groups per 1000 carbons, is larger than those for LLDPE and HDPE and that the number of methyl groups per 1000 carbon atoms is nearly independent<sup>16</sup> of MW. The present results are in agreement with the chemical nature of HP-LDPE<sup>17,18</sup>.

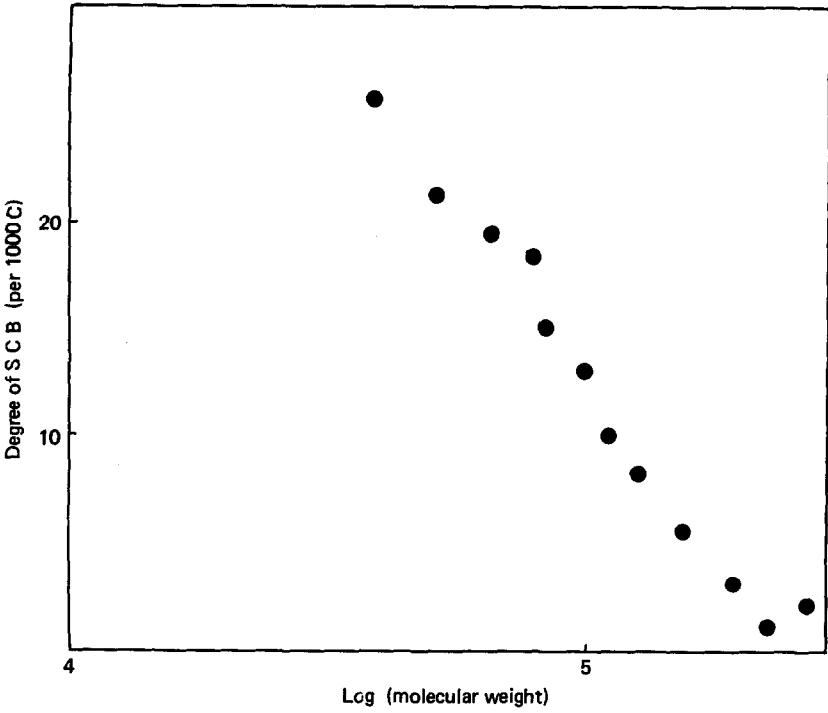


Fig. 3. Degree of short-chain branching per 1000 carbon atoms of LLDPE-A as a function of molecular weight distribution determined by the TREF method.

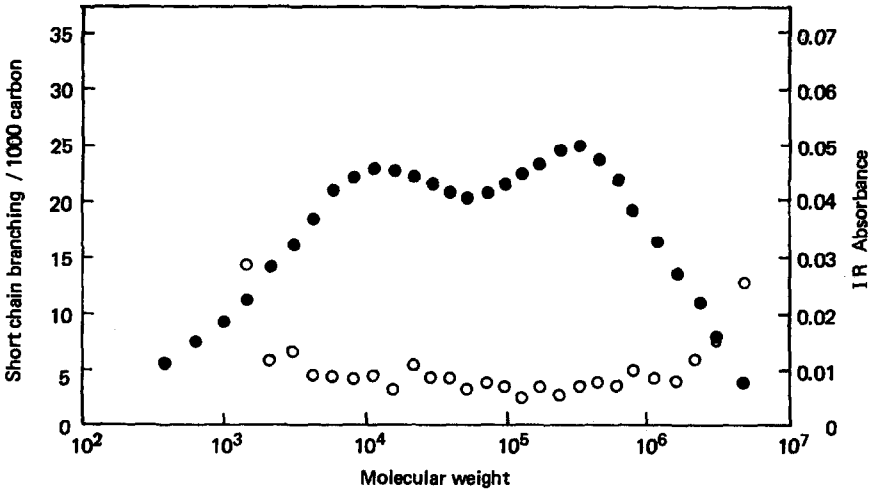


Fig. 4. Extent of short-chain branching per 1000 carbon atoms of HDPE-B as a function of molecular weight (○, left-hand ordinate) and GPC curve as measured by IR absorbance (●, right-hand ordinate).



## CONCLUSION

The GPC-FT-IR method was found to be an excellent substitute for the SGEF-NMR method and can differentiate several kinds of LLDPE and HDPE according to the SCB. However, the GPC-FT-IR method, which is a two-dimensional analysis, gives only the variation of the average chemical composition, such as the ratio of co-monomer to ethylene monomer as a function of MW. Even with such a limitation, the method can differentiate several types of polyethylene for industrial purposes.

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