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**LONG AND SHORT CHAIN BRANCHING
FREQUENCY IN LOW DENSITY
POLYETHYLENE (LDPE)**

Prepared for publication by

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Long and short chain branching frequency in low density polyethylene (LDPE)

Abstract - Five different laboratories have collaborated in a research programme on determination of the branching frequency in a LDPE sample.

Size exclusion chromatography (SEC), SEC-on-line viscosity (QLV) measurements, DSC-, NMR-, viscosity measurements, as well as SEC-on-line low angle laser light scattering (LALLS) measurements and off-line LALLS measurements, were performed on both the whole sample and on fractions. The fractions were obtained by temperature rising elution fractionation (TREF) and by liquid-liquid phase separation (L-L), respectively.

Different long chain branching (LCB)-parameters can be derived. Their differences were explained and some of them were used in this investigation. Also, different B-values in the expression $g' = g^B$ were used and discussed. A B-value of 0.9 was obtained for the global sample.

The conclusion of the fractionation work on the LDPE was that TREF fractionates according to short chain branching (SCB) and that L-L fractionates according to LCB.

INTRODUCTION

In low density polyethylene (LDPE) both long and short side chains are present. The number and length of these side chains and hence the branching density varies over the molecules and molar mass distribution. It is believed that the heterogeneity of these complex structures influence the morphology and the rheological properties of the polymer.

During the past fifteen years the Working Party on the Molecular Characterization of Commercial Polymers has investigated several LDPE samples in order to improve the characterization methods where the LCB-concept has to be considered. Although a closer agreement between the measured values has been reported (Ref. 1) compared to the earliest reports (Ref. 2,3) any detailed information about the complex structure of branching has not resulted due to analytical difficulties.

In order to make progress with this problem a small subgroup within the Working Party was formed in 1983. The members of the subgroup decided to fractionate a LDPE-sample according to different techniques, to characterize the whole polymer and the fractions with different powerful techniques and to determine the amount of long chain branching (LCB) as a function of molecular mass according to different procedures.

This report describes the contributions from some (new) members of the Working Party for the whole polymer as well as the contributions from the subgroup for the whole polymer, the fractions and the fractionation methods.

MATERIAL

Sample β , a commercial long chain branched LDPE, was provided by DSM. According to the earlier results obtained by different methods by different laboratories (Ref. 1) the sample was found to be sufficiently homogenous. In table 1 the melt index and density mean values, as well as some other mean values, are given. The superscripts and the subscripts in this table indicate the maximum deviation to the higher and lower side respectively.

FRACTIONATION METHODS

In order to characterize the branching of LDPE very careful analysis of global samples are normally not sufficient, but the new on-line measurements also mentioned in this report, are of much help. For this purpose fractionation of the global sample into smaller fractions is necessary.

Most of the fractionation methods are time consuming, so they are seldom applied. However, fractionation procedures have been performed on LD-polyethylenes by Wild et. al. (Ref. 4-5), Bergström et Avela (Ref. 6) and Nakano and Goto (Ref. 7) according to the temperature

TABLE 1. Melt index, density, methyl content and molecular characterization of LDPE- β -sample.

Melt index (g/10')	2.2
Density (kg/m ³)	923.6
Methyl content by IR (CH ₃ /1000C)	22.6
Apparent molecular mass (by SEC) M_n^* (kg/mole)	22 ⁺⁹ ₋₇
M_w^* (kg/mole)	97 ⁺¹¹ ₋₁₁
Absolute molecular mass (Osmometry) M_n (kg/mole)	25.4 ⁺¹ ₋₂
(Light Scattering) \bar{M}_w (kg/mole)	191 ⁺⁵ ₋₄₉
Intrinsic viscosity (TCB, 135°C) (dl/g)	0.91 ^{+0.03} _{-0.03}

rising elution fractionation (TREF) method, by Holtrup (Ref. 8) using a direct extraction method, by Constantin and Hert (Ref. 9) as well as by Mindner and Berger (Ref. 10) using preparative steric exclusion chromatography (SEC). Pennings (Ref. 11) has described a TREF fractionation method on fibers and Koningsveld and Staverman (Ref. 12) a liquid-liquid phase separation procedure.

In this investigation a preparative TREF-fractionation (Wild et. al.) and a liquid-liquid (L-L) phase separation have been performed on the LDPE- β sample. The fractions of both TREF and L-L methods were characterized using different methods such as SEC, Light-Scattering, viscosity, infrared spectroscopy, DSC and NMR.

Temperature rising elution fractionation (TREF) procedure

About 3 g polymer sample was dissolved in xylene at 120 °C at a concentration of 1 %. Then a column filled with Chromosorb P was loaded from the top and the crystallisation was performed decreasing the temperature from 90 °C to 50 °C at a rate of 1 °C/h. The elution step was started pumping xylene through the column at a flow rate of 20 ml/min while increasing the temperature at a rate of 9.6 °C/h. Altogether 25 fractions were obtained and the polymer was precipitated when methanol was added to the cooled solutions. All fraction-solutions were filtrated using a Macherey and Nagel-filter (MN 1674) and the dried polymer residues were weighed.

L-L fractionation

The L-L fractionation on LDPE- β has been performed as follows:

10 g of the sample is dissolved in 2000 ml of p-xylene and heated at 134 °C for 24 hours with stirring, 440 ml of tri-ethylene glycol (TEG) are added, and after one hour stirring is stopped and the solvent is allowed to separate into a dilute and concentrated phase. After 16 hours the lower (dilute) phase is drained, concentrated to 100 ml in a rotavapor and poured into 2500 ml of cold methanol. The precipitate is filtered, washed with methanol and dried in vacuum at room temperature for 3 days (first fraction). The upper (concentrated) layer is diluted to 2000 ml, with p-xylene, again TEG is added (500 ml) and the above mentioned procedure is repeated to obtain the second fraction. In this way ten fractions are obtained. The first fraction, being relatively large, is afterwards separated in the same way into two fractions (1a and 1b).

CHARACTERIZATION METHODS FOR WHOLE SAMPLE AND FRACTIONS

Osmometry

M_n was measured by membrane osmometry. Different types of osmometers were used; the membranes used were "Ultracella allerfeinst" and "Schleicher Schuell 08".

Light-scattering

The light-scattering measurements were performed using a Sofica 42000, a Fica 50 or a low angle laser light scattering (LALLS) apparatus Chromatix KMX-6. The solvents used were α -chloro-naphtalene or 1,2,4-trichlorobenzene (TCB), and the temperatures were 135-145 °C.

SEC

The SEC-measurements were mainly performed at 135-140 °C, using the Waters 200 apparatus and TCB as eluent. Some laboratories also used the Waters 150 C for some measurements. Polystyrene crosslinked with divinylbenzene was used as column material in all cases.

Off-line and SEC on-line viscosity measurements

The intrinsic viscosity measurements were performed at 135 °C using TCB or decalin solvent. The instruments were of the Ubbelohde type. Some of the participants used a SEC/On-Line Viscosity (OLV) system where a FICA-viscometer was connected to the Waters 200 SEC-apparatus.

SEC-LALLS

Two of the participating laboratories used the Chromatix KMX-6 LALLS coupled to the Waters 200 SEC-apparatus. The solvent used was TCB at a temperature of 135 °C. In most cases a refractive index increment of $-0.104 \text{ cm}^3/\text{g}$ was used.

Infrared-measurements

The α -SCB- (Short Chain Branching) amounts calculated as $\text{CH}_2/1000 \text{ C}$ were measured at 1378 cm^{-1} from pressed sheets using different types of infrared spectrophotometers.

DSC-measurements

The melting temperatures, crystallization temperatures and heat of fusion were determined by different commercial DSC-apparatus.

NMR-measurements

One participant provided ^{13}C -NMR data obtained from a Varian XL-200 spectrometer at 50.31 MHz. The sample measurements were taken at 100 °C with broad-band decoupling. The polymer solutions ($\approx 8 \%$ by weight) were prepared in TCB with 20 % benzene- d_6 to provide the deuterium lock.

LONG CHAIN BRANCHING OF POLYMERS

The theory and measurements of long chain branching has been described by several authors (Ref. 13-20) and therefore only the theory connected to the special interests of the Working Party will be overviewed.

The principle of universal calibration (Ref. 21) states that molecules with the same hydrodynamic volume have the same elution volume when studied by SEC. A branched molecule has a smaller hydrodynamic volume than a linear molecule with the same molecular mass. The elution volume of a branched molecule will correspond to a linear molecule with a lower apparent molecular mass M . As the hydrodynamic volume depends both on molecular mass and degree and type of branching, at least one more size-related parameter, e.g. intrinsic viscosity (η), or M , is requested besides the data obtained by SEC.

The decrease in size is described by the parameter g , defined as

$$g = \frac{\langle R^2 \rangle_{g \text{ br}}}{\langle R^2 \rangle_{g \text{ lin}}} \quad (1)$$

where $\langle R^2 \rangle_{g \text{ br}}$ is the mean square radius of gyration of the branched molecule, and $\langle R^2 \rangle_{g \text{ lin}}$ is the corresponding quantity for a linear molecule with the same molecular mass in the unperturbed state.

Due to experimental difficulties mostly the expressions

$$g' = g^B \quad (2)$$

and

$$g' = \frac{[\eta]_{\text{br}}}{[\eta]_{\text{lin}}} \quad (3)$$

have been used, where $(\eta)_{\text{br}}$ is the intrinsic viscosity of the branched sample and $(\eta)_{\text{lin}}$ is the intrinsic viscosity of a linear sample of the same molecular mass distribution. To calculate the η_{lin} it is, strictly speaking, necessary to know the whole molecular mass distribution, but knowledge of M_w and the width of the distribution (M_w/M_n) is sufficient to a good approximation (Ref. 13).

B includes the effects of all unknown factors. Different values of B have been found theoretically and experimentally, but they all vary between 0.5 and 1.5.

Suggestions how to obtain a correct molecular mass distribution (MWD) curve and a measure of g' for a branched polymer have been proposed. Drott and Mendelson (Ref. 22-23) and Kurata et. al. (Ref. 24) developed iterative techniques, which resulted in a correct MWD and values of the LCB-amount expressed as branching amount per molecular mass unit. Later Scholte and Meijerink (Ref. 13) reported valuable theoretical considerations with respect to the parameter g' .

Intrinsic viscosity of the effluent from SEC can be measured semi-continuously by installing an Ubbelohde viscometer on-line with the SEC-equipment (Ref. 25-27). The effluent time will give the viscosity for each fraction with this method. Another method applies the pressure drop over a capillary, which gives a possibility to record the viscosity continuously (Ref. 28-29). Some new applications of the pressure drop principle have recently been published (Ref. 30-31).

It was shown (Ref. 13) that a branching parameter g'_{III} can be obtained according to

$$g'_{III} = \left(\frac{[\eta]_{\text{exp}}}{[\eta]^*} \right)^{\alpha+1} \quad (4)$$

where the apparent intrinsic viscosity, $(\eta)^*$, of linear molecules with the same elution volume is obtained from M^* , according to the linear calibration and the appropriate Mark-Houwink relation, $(\eta)=K \cdot M^\alpha$, and $(\eta)_{\text{exp}}$ is the measured intrinsic viscosity. If LALLS is used on-line with the SEC-equipment, the absolute molecular mass can be measured continuously. Then another branching parameter can be defined (Ref. 13):

$$g'_{II} = \left(\frac{M^*}{M} \right)^{\alpha+1} \quad (5)$$

In this case the apparent molecular mass is taken from the linear calibration. Because both g'_{III} and g'_{II} are affected by band broadening in the SEC-columns this effect has to be taken into consideration.

There is still a possibility to measure g' using a parameter g'_I , defined as

$$g'_I = \frac{[\eta]_{\text{exp}}}{[\eta]_{\text{lin}}} \quad (6)$$

where $(\eta)_{\text{exp}}$ is measured directly from the on-line viscometer and $(\eta)_{\text{lin}}$ is calculated from the LALLS-determination of M_w by a Mark-Houwink relation for narrow molecular mass fractions

$$[\eta]_{\text{lin}} = K \cdot M_w^\alpha \quad \square \quad \text{approx.} \quad K \cdot M_w^\alpha \quad (7)$$

A proper value of the exponent B in the equation (2) is essential in order to obtain true LCB-values from the g'_I -results.

The most useful expressions of LCB that are discussed in this report are g'_I and LCB/1000 C. These are related to g in equation (1) according to (8) for trifunctional random branching in monodisperse polymers and to (9) for trifunctional polydisperse polymers respectively (Ref. 20), where m is the number average number and

$$g = \left[\left(1 + \frac{m}{7} \right)^{1/2} + \frac{4}{9} \frac{m}{\pi} \right]^{-1/2} \quad (8)$$

$$\langle g \rangle_w = \frac{6}{n_w} \left[\frac{1}{2} \frac{(2 + n_w)^{1/2}}{n_w^{1/2}} \ln \left(\frac{(2 + n_w)^{1/2} + (n_w)^{1/2}}{(2 + n_w)^{1/2} - (n_w)^{1/2}} \right) - 1 \right] \quad (9)$$

where n_w is the weight average number of branch points per molecule.

$$n_w \quad \square \quad \lambda^* M \quad (10)$$

$$\text{LCB}/1000 C = \frac{n_w \cdot 14000}{M} \quad (11)$$

where $M = M_w$ \square absolute molecular mass from LALLS. The ratio of number of branch points per molecule n_w to molecular mass is expressed by lambda (λ) (Ref. 22). The value of n_w for molecules of measured molecular mass M can be obtained by solving equation (9) with the particular value of g obtained from equation (5) (Ref. 33).

RESULTS AND DISCUSSION

Complementary work on the whole LDPE-sample

Reexamination of the original sample was performed, using partly new kinds of equipment, such as on-line viscometry (OLV) and low angle light scattering techniques (LALLS), in combination with SEC-instruments. The new results from the individual laboratories are shown in table 2.

When comparing these data with table 1, it is found that a rather good agreement exists between the new and the old results, with the exception of the off-line light scattering results.

Measurements using ^{13}C -NMR technique resulted in 4.5 ethyl branches per 1000 carbons, 6.0 butyl-, 1.8 pentyl- and 0.8-1.5 branches due to hexyl and higher side chains (plus end chain). The last results were calculated from the ratio of the peak area for the resonance at $\delta = 32.19$ (heptyl +) to the total area.

The branching parameters g'_I and g'_{III} expressed by the equations (6) and (4) respectively, were calculated for the whole sample by five laboratories. Two laboratories calculated g' as function of molecular mass using equation (8) and a B-value of 1.0 and 0.5 respectively. The g'_I -values agree reasonably well in the middle molecular mass region, but not at the higher and lower ends (fig. 1).

As seen in fig. 2 the g'_{III} -values increase towards lower molecular masses. As the molecules with a high molecular mass in practice are more strongly branched than the low molecular weight polymers, the following relation should generally be valid (Ref. 32):

$$g'_{II} < g'_I < g'_{III} < 1 \quad (12)$$

A comparison of the results in fig. 1 and fig. 2 confirm this and the three g' -factors will differ still more significantly in the case of broad MWD. In the case of a broad polydisperse polymer, g'_I is the overall LCB index of the sample with all molecular masses contributing, the highest molecular mass to a somewhat greater extent, and g'_{III} gives an indication of the branching in the middle part of the distribution.

In fig. 3 the values of LCB/1000 C, are calculated as function of molecular mass from the equations (8)-(11), using two different estimates for B. As expected, it is seen that lower B-values give higher LCB-amounts within the whole molecular mass range.

Fractionation results

The tables 3-4 show the results from the analysis of the TREF-fractions.

Relatively good agreements are found between the results of the molecular masses from the different laboratories. The SEC-LALLS M_w -values differ considerably from the M_w -values, which are not corrected for LCB.

TABLE 2. Intrinsic viscosity $[\eta]$ (TCB, 135°C), apparent molecular mass from SEC (M_n^*), absolute molecular masses from osmometry (M_n) and from light scattering (M_w -LS) and from SEC-LALLS (M_w -SEC-LALLS). Results for the original LDPE sample.

$[\eta]$ (dl/g)	M_n^* (kg/mole)	M_w^* (kg/mole)	M_n (kg/mole)	M_w -LS ⁽¹⁾ (kg/mole)	M_w -SEC-LALLS (kg/mole)
0.91	19	122		292	223
0.89	16	90	23	225	200
0.92				248	
0.92	20	96	18	160	
		103			
0.92					
0.90 ⁽³⁾	22/25 ⁽²⁾	94/102 ⁽²⁾			163/177 ⁽²⁾
0.92	23	106	25	250	
0.91	23	91	25	250	
0.88	21	110	24		
0.92	21	90			
0.95	15	106		194	
mean					
0.91	20	101	23	231	191

(1) Different solvents

(2) Complementary measurements

(3) Measured on-line with SEC

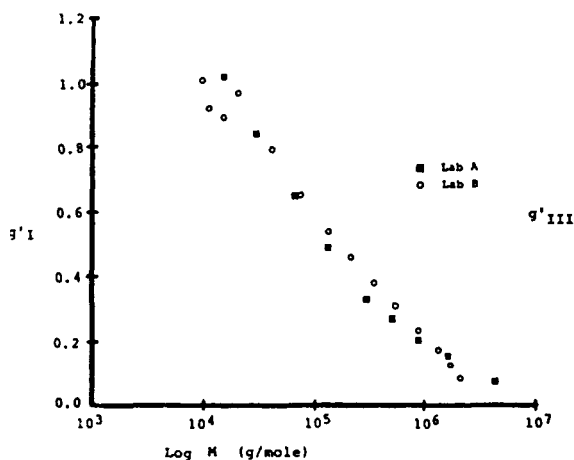


Fig. 1. g'_I given as function of molecular mass.

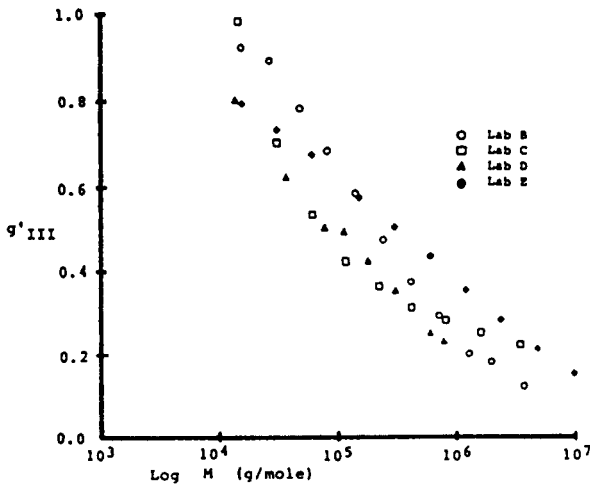


Fig. 2. g'_{III} given as function of molecular mass.

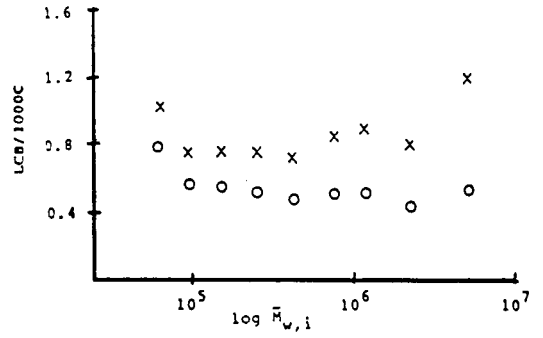


Fig. 3.

Comparison between LCB-results obtained by different exponents B . $\bar{M}_{w,i}$ from SEC-LALLS. X $B=0.7$ O $B=0.85$

LCB/1000C = Number of long chain branches per 1000 carbons.

TABLE 3. TREF-fractions -- Intrinsic viscosity and molecular mass.

Fraction no.	LAB A			LAB B	
	$[\eta]$ (dl/g) On-line (kg/mole) with SEC TCB, 135°C	\bar{M}_n^* (kg/mole)	\bar{M}_w^* (kg/mole)	$\bar{M}_n \cdot 10^{-3}$ SEC-LALLS (kg/mole)	\bar{M}_w^* (kg/mole)
13	0.46	14	34	27	
14	0.46	16	38	41	13 33
17					16 57
18	0.79	25	82	103	20 65
19	0.83	30	85	117	21 75
20	0.84	34	111	137	25 88
21	0.81	30	97	138	26 95
22	0.91	42	115	166	31 117
23	0.96	38	121	205	37 136
24	0.81	32	108	184	28 121
25	1.02	41	125	207	34 123
26	1.07	40	126	226	38 133
27	1.06	44	134	222	40 150
28	1.08	45	127	216	40 142
29	1.17	47	124	207	35 135
30	1.06	51	135	206	37 127
31	1.12	45	115	171	43 109
32	1.03	47	110	153	40 104
33	0.87	48	102	139	41 100
34	0.96	46	102	127	43 111
35	0.97	42	90	122	40 93
36	0.90	44	82	101	38 86
37	0.88	43	80	97	37 77
38	0.78	46	71	83	
Whole sample	0.89	25	102	177	

TABLE 4. TREF-fractions-- DSC-, IR-, and NMR-results from different laboratories.

Fraction no.	LAB A	LAB B	LAB A	LAB B	LAB A	LAB B
	$T_m(2)$ (°C)	$T_m(2)$ (°C)	T_{cr} (°C)	T_{cr} (°C)	IR $CH_3/1000$ C	NMR Branches/1000 C
13	104		95		22	
14	104		96		24	
17	104		94		15	
18	105	106	93	91	21	17
19	107		98		22	
20	108	107	95	93	20	
21	108		94		20	
22	108	108	94	92	21	
23	109		94		14	
24	107		97		10	
25	108		96		18	
26	108	109	96	92	19	
27	110		96		16	
28	110	111	97	93	16	14
29	113		97		14	
30	111	112	97	94	15	
31	114		97		15	
32	111	113	99	95	15	
33	112		100		13	11
34	115	114	100	98	12	
35	113		102		12	
36	114	114	102	100	11	
37	115		103		11	
38						
39	115		105		11	
Whole sample		112		96		

$T_m(2)$ means the melting point of the second scan.

The TREF-method fractionates according to short chain branching (SCB) as can be seen from the results in table 4. The NMR-technique gives results, which are very close to those obtained by IR. The more crystalline species, eluting at higher temperature and showing lower CH₂-content, also show higher melting points.

The results from the L-L phase separation are shown in table 5 and 6. As can be seen from table 5 the L-L-technique fractionates according to molecular mass, but the SCB-amount expressed as CH₂/1000 C is rather constant. Thus there are remarkable differences between the fractions obtained in this investigation by the two fractionation methods.

Long chain branching (LCB) in the fractions

The main interest was to decide which fractionation type is the best to describe LCB in LDPE. Also some other questions concerning LCB, LDPE, SEC, viscometry and LALLS have arisen.

TREF

The original chromatogram obtained from the SEC-RI (refractive index) measurements and SEC-on-line LALLS measurements respectively are compared in figure 4.

According to the figure it seems that the molecular size distribution according to the refractive index measurements is much narrower for the fraction 38 than for fraction 18. However, the LALLS-signal in most cases gives a broader distribution. The LALLS-detector already records material with high molecular masses, when the concentration detector (RI) does not better detect such material (Ref. 14).

TREF does not seem to fractionate very well according to long chain branching. When the amounts of LCB per 1000 carbons were calculated with a B-value of 0.7 according to equation (8) and plotted against the molecular weights of the SEC-LALLS fractions, the fractions 18 and 34 showed a bigger heterogeneity compared to the middle fractions.

Liquid-liquid phase separation (L-L)

Examples of MWDs of the L-L-fractions are shown in fig. 5. Evidently there is a good separation according to molecular mass. The enormous response from LALLS on the fraction 10 is due to the sensitivity towards concentration time's molecular mass. As can be seen from table 5 L-L fractionates according to LCB, which is also demonstrated if we use the results in table 6 and plot λ versus M_w (fig. 6). Exactly the same tendencies are found for the same fractions at another laboratory when λ , determined according to the Drott-Mendelson method with B = 0.7 and the Mark-Houwink constants K = 4.06 · 10⁻² and α = 0.725 is plotted versus M_w from SEC-LALLS (fig. 6).

TABLE 5. Liquid-liquid phase separation -- Intrinsic viscosity and molecular mass. Different laboratories.

Fraction No.	Weight (g)	On-line		\bar{M}_w^*	\bar{M}_w^*	LAB A	LAB B
		$[\eta]_{dec}^{135}$ (dl/g)	$[\eta]_{TCB}^{135}$ (dl/g)			\bar{M}_w SEC-LALLS	\bar{M}_w SEC-LALLS
(1) [∇]	(3.19)						
1a	2.02	0.37		18			
1b	0.55	0.93		56			
2	0.47	0.43	0.46		44 (37)	32	52 (53)
3	0.60	0.71		42			
4	0.53	0.82	0.75		61 (65)	64	62 (52)
5	0.43	0.85	0.73		64 (64)	60	78 (60)
6	0.63	1.04		71			
7	0.84	1.20	0.96		93 (96)	103	100 (95)
8	1.02	1.36		120			
9	1.46	1.92		210			
10	0.47	2.22	1.62		439 (447)	1500	1312 (1088)
Total	9.02						
Whole sample		1.06	0.91	90	119 (108)	191	173 (170)

() = additional measurements
[∇] = the first fraction, being relatively large, is afterwards separated in the same way into two fractions, 1a and 1b.

Note: Molecular mass given as kg/mole.

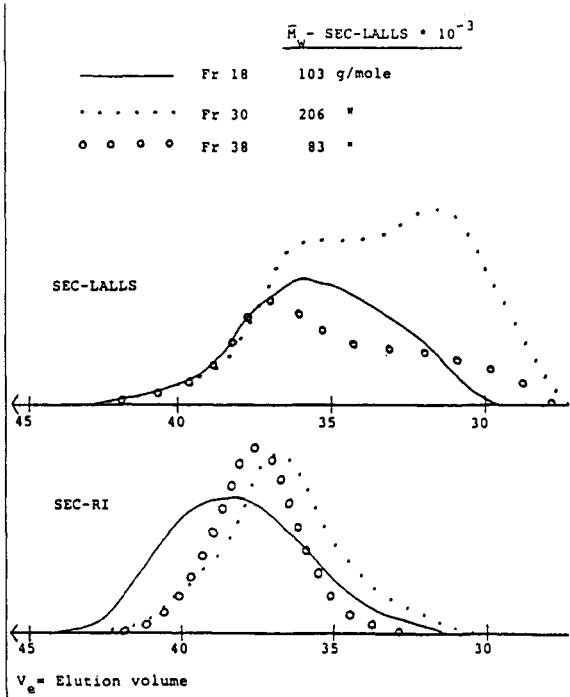


Fig. 4. TREF-fractions. Original SEC-RI and SEC-LALLS-chromatograms.

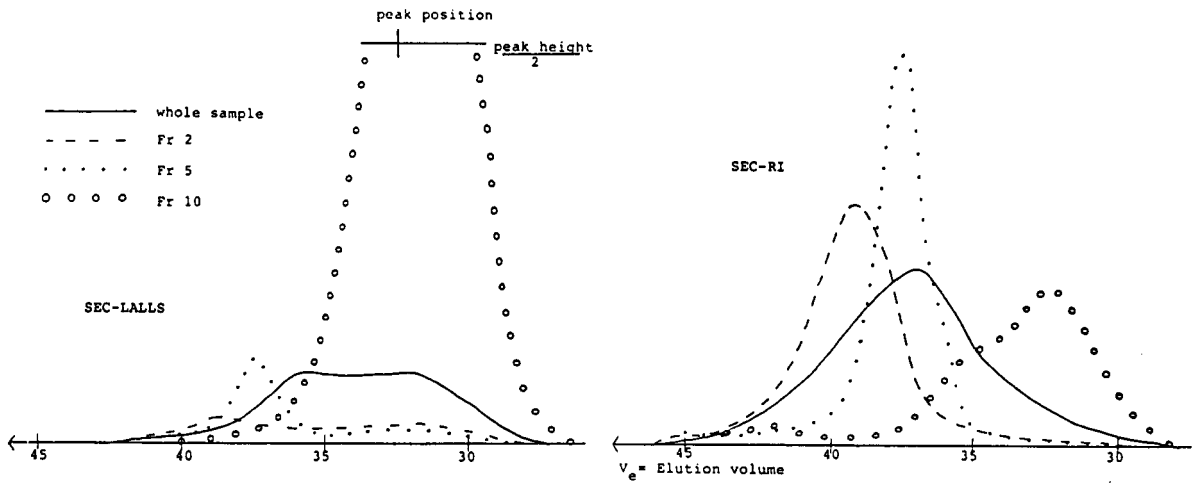


Fig. 5 . L-L-fractions. Original SEC-RI and SEC-LALLS-chromatograms.

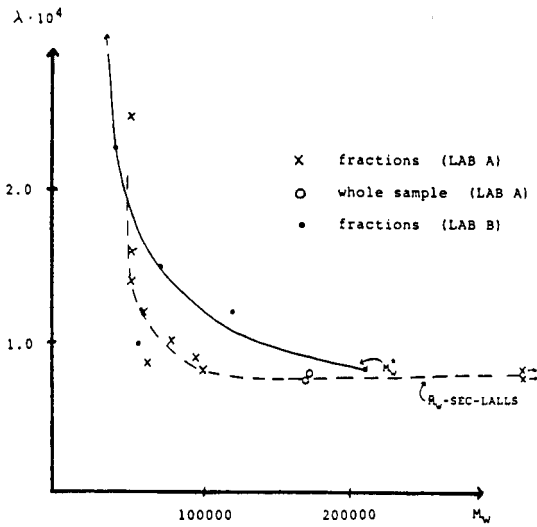


Fig. 6 . L-L-fractions. LCB-parameter λ against molecular mass . (Different laboratories)

TABLE 6. Liquid-Liquid phase separation - IR, DSC and LCB results - laboratory A .

Fraction No.	CH ₂ /1000 C	T _m (°C)	T _{cr} (°C)	M _w [*] (kg/mole)	g' III	$\lambda \cdot 10^{-4}$	Number of LCB /1000 C
1a	21.5	101/111/115	99	18	0.52	5.07	7.1
1b	16.4	111.5	98	56	0.64	0.98	1.4
2		101/111/114.5	100				
3	18.6	112-114	96.5	42	0.52	2.27	3.2
4		112	95.5				
5		111	96				
6	18.1	110.5	94	71	0.50	1.49	2.1
7		110	92.5				
8	18.2	109	92	120	0.43	1.19	1.7
9	18.6	107.5	92	210	0.395	0.81	1.1
10		107	93				

$$g'_{III} = \left[\frac{(\eta)_{dec/1.17}}{(\eta)^*} \right]^{1.725} \quad \text{according to eq. (4)}$$

Note 1: η_{dec} = viscosity measured at 135 °C with decalin as solvent. A conversion factor 1.17 has been found for the ratio $[\eta]_{dec}^{135} / [\eta]_{ICB}^{135}$ (Ref. 34).

Note 2: The LCB-parameter λ expresses the number of branching points/molecule/molecular mass.

TABLE 7. Differences between g'_I and g'_{III} .
Sample β .

SEC elution volume	g'_I from OLV and SEC-LALLS	g'_{III} from OLV and SEC calibration curve
30	0.08	0.02
31	0.12	0.05
32	0.17	0.10
33	0.23	0.16
34	0.31	0.23
35	0.38	0.31
36	0.46	0.40
37	0.54	0.51
38	0.65	0.59
39	0.79	0.71
40	0.97	0.77
41	0.89	0.87
42	0.92	(1.20)
43	1.01	(2.82)

OLV = On-line viscometry

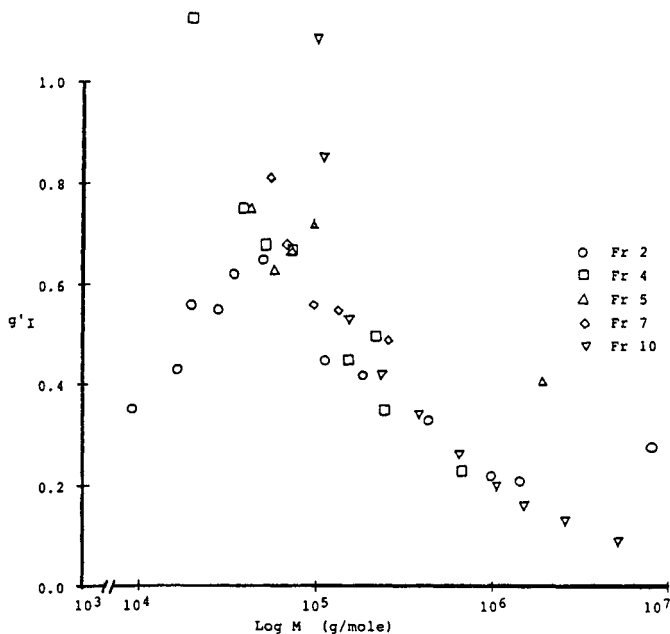


Fig. 7. g'_I of L-L fractions presented as function of molecular mass.

Complementary work on the molecular masses and λ s are shown in the tables 7 and 8. The results are obtained using different B- and K-values.

Fig. 7 shows g'_I as function of molecular mass for the L-L fractions measured by SEC-LALLS and table 7 presents g'_I for the whole sample measured by SEC-LALLS or g'_{III} measured by SEC-OLV respectively.

The absolute g'_I -results correlate to g'_{III} , although there are differences in the absolute values. Obviously there are difficulties with the measurements of g' along the MWD, especially for the middle fractions. This phenomenon has been found several times, when reanalysing the same samples. It seems that conclusions about LCB for fractions should be drawn from average LCB-parameters until the analysing methods become even more improved than they are today. However, for the whole sample, g'_I is a reliable LCB-parameter.

ADDITIONAL RESEARCHES

Is LCB constant, decreasing or increasing with molecular mass for an ordinary LDPE? During this project some participants produced several interesting findings. One of them is shown in fig. 8 where the importance of a proper choice for the exponent B is clearly demonstrated.

The exponent B may also affect the M_w -results considerably. Fig. 9 shows M_w calculated from LALLS on-line with SEC compared to estimates from the Drott-Mendelson-method using different values for B. The conclusion of this comparison is: For the high molecular mass fraction, the SEC-LALLS-result is very close to the SEC-result calculated with $B = 0.5$ while for the low molecular mass fractions $B = 0.9$ seems to be the better choice. For the whole polymer the SEC-LALLS-result is quite close to $B = 0.9$.

Also the choice of Mark-Houwink constants for polyethylene in TCB, at 135 °C, has been discussed. In order to get comparable results from different laboratories, the values of K and α have to be fixed and some suggestions have been formulated to that purpose. The latest one is to use $K = 4.06 \cdot 10^{-4}$ and $\alpha = 0.725$. Tables 8-9 show the use of different K-values in combination with different B-values.

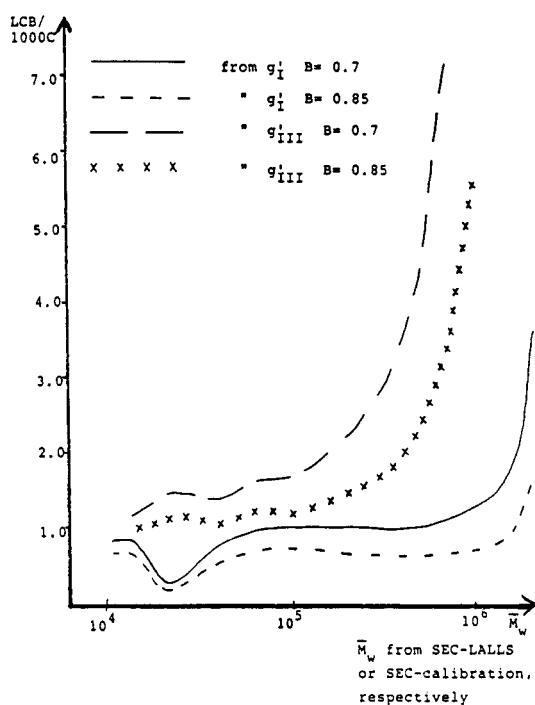


Fig. 8. Different calculations of LCB/1000C for sample β . LCB/1000C = Number of long chain branches per 1000 carbons.

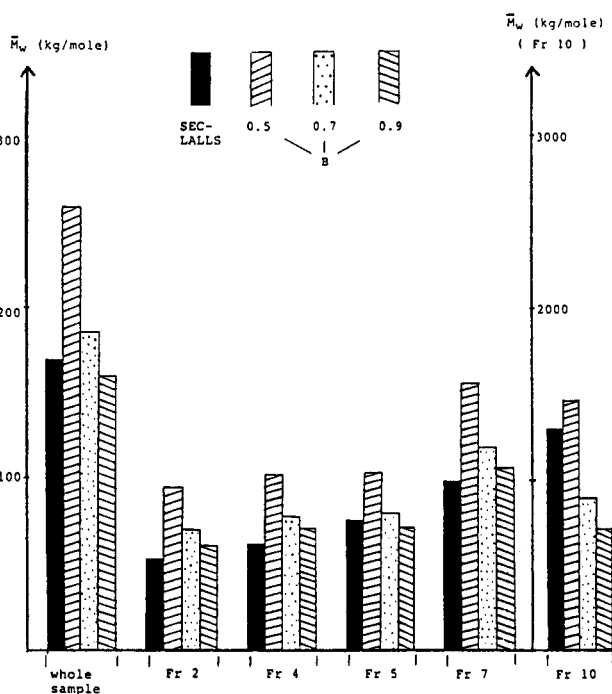


Fig. 9. L-L-fractionation of sample β . \bar{M}_w from SEC-LALLS and from Drott-Mendelson-procedure with different exponents B.

TABLE 8. Sample β . L-L fractionation. The use of different B and K values when the value of the constant α in the Mark-Houwink equation = 0.725 in all calculations. The effect on the molecular mass (Drott-Mendelson procedure).

Sample	Mark-H. const. $K \times 10^{+4}$ (dl/g)	B = 0.5		B = 0.7		B = 0.9		B = 1.0	
		\bar{M}_w (kg/mole)	\bar{M}_w (kg/mole)	\bar{M}_w (kg/mole)	\bar{M}_w (kg/mole)	\bar{M}_w (kg/mole)	\bar{M}_w (kg/mole)	\bar{M}_w (kg/mole)	\bar{M}_w (kg/mole)
Whole	4.6	17.8	259	16.7	186	16.4	160	16.3	151
	4.06	17.3	225	16.5	169	16.2	148	16.2	142
L-L: Fr 2	4.6	11.3	97	10.3	71	10.1	61	10.0	58
	4.06	10.8	84	10.1	64	9.9	56	9.9	54
Fr 4	4.6	22.6	103	20.9	80	20.3	73	20.1	70
	4.06	21.5	89	20.5	73	20.0	68	19.9	66
Fr 5	4.6	14.4	105	13.7	81	13.5	73	13.4	70
	4.06	14.0	92	13.5	75	13.3	68	13.3	67
Fr 7	4.6	17.4	157	16.7	120	16.4	108	16.3	104
	4.06	17.0	138	16.5	111	16.3	103	16.3	100
Fr 10	4.6	14.0	1462	13.5	885	13.4	714	13.4	665
	4.06	13.8	1288	13.5	816	13.4	675	13.4	634

TABLE 9. Sample β . L-L-fractionation.

The use of different B and K values when the value of α is 0.725.
The effect on LCB (λ). (Drott-Mendelson procedure)¹⁾
All K-values should be multiplied by 10^{-4} .

Sample	Mark-H. CONST. K	B=0.5 $\lambda \cdot 10^4$	B=0.7 $\lambda \cdot 10^4$	B=0.9 $\lambda \cdot 10^4$	B=1.0 $\lambda \cdot 10^4$
Whole	4.6	4.0	1.10	0.56	0.43
	4.06	2.4	0.73	0.38	0.30
L-L:					
Fr 2	4.6	8.6	2.60	1.30	1.00
	4.06	5.0	1.60	0.87	0.69
Fr 4	4.6	4.1	1.40	0.76	0.60
	4.06	2.3	0.85	0.49	0.39
Fr 5	4.6	5.0	1.62	0.88	0.70
	4.06	2.9	1.00	0.59	0.48
Fr 7	4.6	3.9	1.20	0.66	0.52
	4.06	2.3	0.80	0.45	0.36
Fr 10	4.6	5.7	1.06	0.46	0.34
	4.06	3.8	0.79	0.36	0.27

1) According to Drott and Mendelson (Ref. 22) λ is the number of branching points/molecule/molecular mass.

TABLE 10. Comparison of results obtained using silver and asbestos filters, respectively. Sample β . \bar{M}_w -SEC corrected for LCB with B=0.7 and B=1.0.

	$[\eta]$ on-line with SEC (dl/g)	\bar{M}_w (kg/mole)	$\lambda \cdot 10^4$ ¹⁾
Asb.-filt. B=0.7	0.86	181	0.83
Ag-filt. B=0.7	0.87	171	0.78
Asb.-filt. B=1.0	0.86	153	0.34
Ag-filt. B=1.0	0.87	146	0.32

1) The branching density λ was determined with the Drott-Mendelson iterative process (Ref. 22) and expresses the number of branching points/molecule/molecular mass.

TABLE 11. Summary of SEC-LALLS -results (\bar{M}_w as kg/mole) for sample and its L-L fractions, using different dn/dc 's and different A_2 's

	$dn/dc = -0.094 \text{ cm}^3/\text{g}$ $A_2 = 3 \times 10^{-4} \text{ mole cm}^3/\text{g}$	$dn/dc = -0.104 \text{ cm}^3/\text{g}$ $A_2 = 3 \times 10^{-4} \text{ mole cm}^3/\text{g}$	$dn/dc = -0.104 \text{ cm}^3/\text{g}$ $A_2 = 0 \text{ mole cm}^3/\text{g}$	$dn/dc = -0.104 \text{ cm}^3/\text{g}$ $A_2 = 9.8 \times 10^{-4} \text{ mole cm}^3/\text{g}$
Global sample β				
Asb.-filtr.	220	179	176	
Global sample β				
Ag-filtr.		174	172	179
L-L-fractions				
Ag-filtr.				
Fr 2		53	53	
Fr 4		52	52	
Fr 5	73	60	60	
Fr 7		95	95	
Fr 10	1358	1088	1016	

From a practical point of view, the influence of the method for filtrating the sample before injecting it into the SEC-equipment, has also been investigated. During the past years conflicting results have been obtained when comparing silver- and asbestos filtration. However, one recent test with silver- and asbestos-filter with the same pore-size ($0.45\mu\text{m}$, $0.5\mu\text{m}$), used in the same equipment during the same period gave the results seen in table 10.

During this work it was also demonstrated that the refractive index increment value affects the SEC-LALLS-results to a much larger extent than the value of the second coefficient, A_2 (table 11).

DISCUSSION AND CONCLUSION

The use of new SEC compatible instruments, such as SEC-on-line viscometry and SEC-LALLS, has given new information about branching characteristics of LDPE. Together with fractionation methods, such as temperature rising elution fractionation (TREF) and liquid-liquid phase separation (L-L), a rather complete picture of the short chain branching and long chain branching distribution in the sample is obtained.

The LCB parameter g' can be obtained in three ways and the relation

$$g'_{II} < g'_I < g'_{III} < 1$$

has been established. The value of B in the expression $g' = g^B$ seemed to be 0.9 for the global sample and for the low molecular mass fractions. For high molecular mass fractions SEC-LALLS measurements gave very similar results compared to off-line SEC-measurements in the case when a B -value of 0.5 was used. The TREF procedure mainly fractionates according to SCB, whereas L-L fractionates according to molecular mass and LCB. The choice of the right value for the refractive index increment dn/dc in the LALLS measurements is important in order to get reliable results.

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