Long chain branching in low density polyethylene: 1. Molecular structure

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Commercial grade low density polyethylenes (LDPE), manufactured by conventional and modified tubular and vessel reactors have been investigated in order to point out the correlations between rheological behaviour and chain structure i.e. their long chain branching (*LCB*). Preparative gel permeation chromatography has been used to obtain narrow polymer fractions ready for both structural and rheological evaluation. The long chain branching investigation, reported in this first paper, has been performed by viscometric and light scattering measurements. The results indicate that the manufacturing technologies chosen mostly influence the *LCB* of the polymers.

INTRODUCTION

A detailed knowledge of the peculiar structure of polymers is required to be able to connect flow mechanism and synthesis parameters. It is now experimentally confirmed that the rheological behaviour of polymeric materials is affected by the molecular structure, i.e. molecular weight (*MW*), molecular weight distribution (*MWD*) and long chain branching (*LCB*). In spite of this the theoretical treatment of such aspects of the problem is far from being less exhaustive, even though considerable progress has been achieved in these last few years. The investigation reported here, which concerns the evaluation of the molecular structural parameters of low density polyethylene (LDPE) is the first essential step in establishing and interpreting the correlations between synthesis conditions and application properties of the product; the latter will be investigated in subsequent papers.

EXPERIMENTAL

Samples

The samples used in the present investigation were high pressure polyethylenes produced in industrial plants and synthesized using different technologies such as tubular and vessel type and their modifications. The characteristics of the examined samples are summarized in *Table 1*. A linear polyethylene sample with known characteristics, used as standard in many laboratories, was chosen as reference.

Fractionation

Polyethylene samples were fractionated by gel permeation chromatography with an Anaprep apparatus of Waters Associates, equipped with two columns, 2.4 inches diameter and 4 feet length, packed with Styragel. Such columns exhibited nominal dimensions of pores of 5×10^3–1.5×10^4 Å and 5×10^4–1.5×10^5 Å. The temperature of the oven, into which the columns were placed, was kept constant at 135°C, the solvent used for elution was orthodichlorobenzene (ODCB). A 1% polymer solution (100 cc) was injected during each fractionation cycle; 14–15 fractionations were carried out for each sample. By conveniently adjusting the eluate collection device, the samples were separated into about 20 fractions. Each of these was then concentrated at a reduced pressure up to 1/10 of the initial volume and later recovered by precipitation with methanol.

No serious degradation occurred during the run as was proved by comparing the intrinsic viscosity of the original sample with the sum of the product of the intrinsic viscosities $[\bar{\eta}]_i$ by the relating weight fraction W_i of each polymer fraction ($\Sigma w_i[\eta]_i$).

Table 1 Physico-chemical properties of raw samples

Sample	Process	Density at 23°C	*MFR*	$[\eta]^{135°C}_{ODCB}$	$\bar{M}_w \times 10^{-3}$	$\frac{A_w}{A_n}$
T-2	tubular	0.9172	1.57	0.88	360	5.7
T-3	tubular	0.9176	0.24	1.04	550	5.7
TM-2	mod. tub.	0.9234	2.13	0.83	135	4.1
V-1	vessel	0.9128	84.0	0.66	210	6.6
V-2	vessel	0.9144	22.4	0.83	340	8.8
V-3	vessel	0.9156	6.58	0.96	420	9.6
V-4	vessel	0.9176	1.19	1.08	690	9.4
VM-1	mod. vess.	0.9198	1.75	0.91	140	4.5
VM-3	mod. vess.	0.9211	0.25	1.12	275	4.7
VM-5	mod. vess.	0.9217	0.24	1.14	600	6.6
1475*NBS*	linear	0.9780	15.1	1.00	52	3.0

T = samples obtained by tubular process
V = samples obtained by vessel process
TM, VM = samples respectively obtained by a modified tubular and vessel process

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Table 2 Physico-chemical properties of the raw products and of the fractions of samples, linear (NBS 1475) and LDPE, synthesized by a tubular process

Samples	$[\bar{\eta}]^{135°C}_{ODCB}$	$\bar{M}_w \times 10^{-3}$	$A_2 \times 10^4$ ($cm^3 mol\ g^{-2}$)	R_g (Å)	*MWD*	*g*	*nw*	$\lambda^{1/2} \times 10^2$	CH_3/100C	*Tm*(°C)
NBS 1475 Raw	1.00	52			3.0					133
fract. *A*	2.02	115				0.955	0.24	0.146		135
fract. *B*	1.44	70				0.997	0.02	0.056		134
fract. *C*	1.16	49				1.085	0.00	0.000		
fract. *D*	1.00	43				0.974	0.13	0.179		133
T-2 Raw	0.88	360			5.7				3.0	
fract. *A*	2.53	6600	1.30	970		0.004	850.72	1.135		
fract. *B*	2.16	1550	1.61	770		0.025	611.24	1.986		108
fract. *C*	1.60	580	4.05	510		0.057	214.20	1.922	1.48	
fract. *D*	0.98	195				0.104	94.91	2.206		
fract. *E*	0.48	46				0.203	35.50	2.778		
T-3 Raw	1.04	550			5.7				3.2	
fract. *A*	2.37	3100	4.50			0.011	850.72	1.656		
fract. *B*	2.29	1350	5.56			0.034	411.69	1.746		106
fract. *C*	1.60	580	8.30	650		0.057	214.20	1.922	1.24	
fract. *D*	1.18	232	7.55			0.118	80.12	1.858		
fract. *E*	0.57	53	12.67			0.234	28.43	2.316		
TM-2 Raw	0.83	135			4.1					
fract. *A*	1.83	245	5.1	341	1.4	0.262	23.53	0.980		
fract. *B*	1.49	180	7.9	307	1.5	0.271	22.13	1.109	1.42	
fract. *C*	1.08	100	7.7		2.2	0.334	15.24	1.235	1.43	
fract. *D*	0.75	55	13.0		2.2	0.383	11.76	1.462		
fract. *E*	0.63	43	8.7		2.5	0.387	11.52	1.637	1.35	

Viscosimetric measurements

Intrinsic viscosities, $[\bar{\eta}]$, were determined in ODCB at at 135°C by modified Desreux-Bischoff viscometers[11], dimensioned in such a way as to make the kinetic energy correction negligible. Intrinsic viscosities, $[\eta]$, were determined by extrapolation to C=O of the $\eta_{sp/c}$ values, obtained at four different concentrations falling within the 1:–1/2–: –1/3–: –1/4: ratios.

G.p.c. analyses

G.p.c. measurements were carried out by the analytical section of the same Anaprep instrument at 135°C using ODCB as eluent. The fractionation system consisted of a set of four linear columns packed with Styragel, which had a nominal porosity of 10^5 Å.

The calibration curve was determined with linear polyethylene fractions and controlled by analysis of standard samples with an exactly known molecular weight and *MWD*.

Light scattering

Light scattering measurements were carried out in α-chloronaphthalene at 125°C by a photogoniodiffusiometer, Mod. 42000 by Sofica with 5461 Å wavelength non-polarized light. Silicon oil, type 200/50, from Saprochim, with a refractive index of about 1.55 at 125°C was used as the cell thermostating medium.

The solutions were prepared by directly weighing the polymer and the solvent, then maintained at 135°C for one hour. The single concentration sets were suitably chosen for the molecular weight of the fractions to be measured: the solution scattered light intensity had to be about 25% higher than that of the solvent.

All solutions were then filtered under low pressure (<0.1 atm) directly in the cell at 130 ± 2°C using millipore filters (Millipore Filter Corp.) having porosities of 0.45 μ and 0.22 μ, respectively, for the lower molecular weight measurements.

The photogoniodiffusiometer was calibrated with pure benzene checking the resulting calibration with standard samples. The d*n*/d*c* was determined in α-chloronaphthalene at 125°C and, for a wavelength of 5461 Å, it was found to be 0.193 $cm^3\ g^{-1}$.

Density measurements

Density measurements were performed using a gradient column of 2 m long at 23°C following the ASTM-D-1505/68 method.

Melt flow rate

Melt flow rate was determined by a capillary rheometer at constant pressure (CEAST mod. 6540) following the ASTM-D-1238/73 method condition E procedure B.

Short chain branching

Short chain branching (CH_3/1000 C) was determined i.r. spectroscopy, measuring the absorption at 1378 cm^{-1}.

RESULTS AND DISCUSSION

Fractionations on preparative g.p.c. were carried out on a number of LDPE samples, which had been prepared by the two processes most commonly adopted in industrial plants i.e. the tubular (T) and the vessel (V) type ones, and their experimental modifications (TM, VM).

Fractionations were performed in such a way as to obtain amounts of fractions that, in the right range of molecular weights, might be even rheologically characterized by a method arranged for small quantities of material[13].

The structural characterization of the polymer fractions has been made basically by intrinsic viscosity and light

Table 3 Physico-chemical properties of the raw products and of the fractions of LDPE samples, synthesized by the conventional vessel process

Samples		$[\bar{\eta}]^{135°C}_{ODCB}$	$\bar{M}_w$ x 10^{-3}	A_2 x 10^4 (cm^3 mol g^{-2})	R_g (Å)	*MWD*	*g*	*nw*	$\lambda^{1/2}$ x 10^2	CH_3/100C	*Tm*(°C)
V-1	Raw	0.66	210	4.3		6.6				2.29	104
	fract. *A*	1.71	2450	0.84	601	1.7	0.008	850.72	1.863		
	fract. *B*	1.34	725	4.0	366	1.7	0.029	508.27	2.648		
	fract. *C*	0.98	275	4.6	197	1.9	0.063	187.06	2.608	2.38	101
	fract. *D*	0.73	110	5.2		2.2	0.133	67.48	2.477	2.34	104
	fract. E.	0.51	38	6.1		2.4	0.303	18.28	2.194	2.42	106
V-2	Raw	0.83	340	3.4		8.8				2.26	107
	fract. *A*	1.88	2000	1.76	597	1.8	0.013	850.72	2.062	2.46	103
	fract. *B*	1.40	708	2.79	417	1.9	0.033	436.75	2.484	2.47	104
	fract. *C*	1.05	285	5.07	346	2.3	0.069	166.68	2.418	2.65	105
	fract. *D*	0.71	98	7.00	116	2.4	0.149	57.25	2.417	2.70	107
	fract. *E*	0.48	41	14.80		2.3	0.240	27.15	2.573	2.74	109
V-3	Raw	0.96	420			9.6				2.31	
	fract. *A*	1.92	2000	2.0	690	1.6	0.014	850.72	2.062	2.34	
	fract. *B*	1.49	685	3.7	520	2.1	0.039	350.24	2.261		
	fract. *C*	1.10	300	3.9	416	2.3	0.070	162.36	2.326	2.36	
	fract. *D*	0.83	145	5.8	284	2.2	0.115	82.80	2.389	2.40	
	fract. *E*	0.61	61	16.4		2.4	0.218	31.75	2.282		
V-4	Raw	1.08	690			9.4				2.70	
	fract. *A*	2.18	2600	1.60	495		0.012	850.72	1.809		
	fract. *B*	1.49	930	2.63	440		0.025	611.24	2.564		
	fract. *C*	1.07	390	4.55	350		0.045	287.99	2.717		
	fract. *D*	0.76	163	7.00			0.081	133.66	2.864		
	fract. *E*	0.65	103	9.70			0.116	81.97	2.821		

Table 4 Physico-chemical properties of the raw products and of the fractions of LDPE samples synthesized by the modified vessel process

Samples		$[\bar{\eta}]^{135°C}_{ODCB}$	$\bar{M}_w$ x 10^{-3}	A_2 x 10^4 (cm^3 mol g^{-2})	R_g (Å)	*MWD*	*g*	*nw*	$\lambda^{1/2}$ x 10^2	CH_3/100C	*Tm*(°C)
VM-1	Raw	0.91	140			4.5				1.73	112
	fract. *A*	1.75	410	5.3	339	1.5	0.113	84.57	1.436	1.52	108
	fract. *B*	1.32	211	4.8	235	1.8	0.169	47.20	1.496		110
	fract. *C*	0.99	103	8.1	154	2.4	0.269	22.46	1.477		110
	fract. *D*	0.86	83	7.9	179	2.4	0.278	21.28	1.601	1.64	
	fract. *E*	0.74	65	14.4		2.6	0.293	19.40	1.728		112
VM-3	Raw	1.12	275			4.7				2.10	
	fract. *A*	2.43	1850	2.53	620		0.025	627.49	1.842		
	fract. *B*	1.96	690	4.33	420		0.067	174.18	1.589	1.50	
	fract. *C*	1.40	270	6.00			0.133	67.48	1.581		
	fract. *D*	0.96	119	9.30			0.205	35.11	1.718		
	fract. *E*	0.73	77	10.80			0.223	30.66	1.995		
VM-5	Raw	1.14	600			6.6				2.40	
	fract. *A*	2.25	5500	1.14	820		0.004	850.72	1.244		
	fract. *B*	2.15	1450	2.58	580		0.027	547.37	1.943		109
	fract. *C*	1.55	620	4.04	410		0.049	263.12	2.060	1.18	
	fract. *D*	0.90	155	7.80			0.123	75.35	2.205		118
	fract. *E*	0.54	55	9.60			0.199	36.77	2.586		116

scattering measurements which, in addition to the weight-average molecular weight, allow the evaluation of other parameters, such as radius of gyration R_g and second virial coefficient A_2, whose connection with *LCB* has been described[14].

Tables 2, 3 and *4* show the experimental results obtained by such structural characterization. In order to give a simple and homogeneous description, the data, reported here for each sample, concern a small number of fractions, conveniently chosen to avoid any distortion of the average behaviours obtained.

By examining all the experimental values obtained (A_2, R_g, $[\eta]$) that allow the evaluation of *LCB*, the conclusion was drawn, in agreement with other authors[15–19], that the most reliable method, at least for relative comparison, is the viscometric one.

Hence with regard to this investigation, it was decided to choose a method based on measurements of intrinsic viscosity and weight-average molecular weight, determined by light scattering on fractions with as narrow M_w as possible This average value minimizes the influence of the residual polydispersity on the $[\eta]$–M relationships.

This method is based on the relationships suggested by Zimm and Kilb[15] and Zimm and Stockmayer[20], which lead

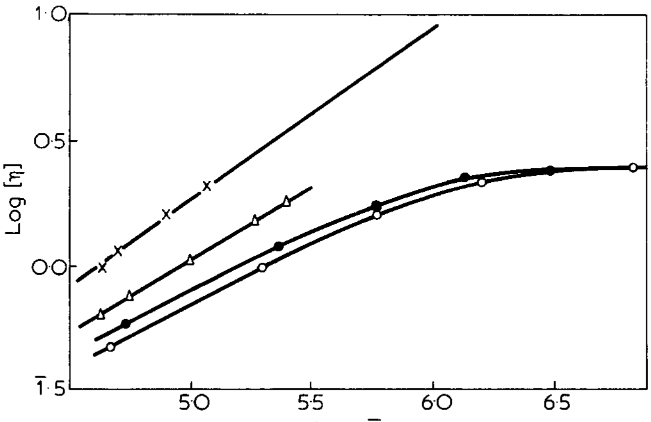

Figure 1 Comparison among the relationships log [η]-log $\bar{M}_w$ of the samples: linear HDPE (X, NBS 1475), LDPE by tubular process (○, *T*-2; ●, *T*-3) and LDPE by modified tubular process (△, *TM*-2)

to the branching frequency through:

$$\frac{[\eta]_{br}}{[\eta]_1} = g^{1/2} \tag{1}$$

$$g = \frac{6}{n_w}\left[\left(\frac{1}{2}\,\frac{2+n_w}{n_w}\right)^{1/2} \ln\frac{(2+n_w)^{1/2}+n_w^{1/2}}{(2+n_w)^{1/2}-n_w^{1/2}} - 1\right] \tag{2}$$

$$\lambda = \frac{n_w}{\bar{M}_w} \tag{3}$$

where $[\eta]_{br}$ and $[\eta]_1$ are the intrinsic viscosities of the branched polymer and that calculated for the linear polymer with the same molecular weight; n_w and g are the number of branches per chain and the branching index, respectively.

The following relationship have been used as a reference for the linear polymer[21]:

$$[\eta]_1 = 4.43 \times 10^{-4} M^{0.725} \tag{4}$$

We have tested its validity, over a narrow range of molecular weight on fractions prepared from the standard linear NBS 1475 [22].

The experimental trends of the [η]–*M* curves for the LDPE samples obtained by a tubular process are shown in *Figure 1.* In spite of the choice of the synthetic conditions intended to obtain products exhibiting different properties (T-3, for pipes; T-2, for films), the conventional tubular process gives polymers with a fairly similar trend in *LCB* over the whole range of molecular weight. Though with a greater data variability, the same conclusions could be drawn from A_2 and R_g values.

The sample prepared by the modified process TM-2 clearly differs in molecular structure. Compared with the corresponding sample T2, not only the weight-average molecular weight, M_w, and consequently the *LCB*, is much lower, but also a considerable sharpening of *MWD* is observed. Notwithstanding the limits imposed by the narrower range of molecular weights (determined by the particular *MWD* of the sample), on which the evaluation has been done, it has been possible to point out a smaller increase in *LCB* with molecular weight, unlike other samples.

From the technological point of view, this result attains considerable importance: it indicates, by conveniently modifying the process, that the molecular structure and consequently the application properties of the polymer can be substantially changed.

The experimental trends in the [η]–*M* relationships concerning the LDPE samples synthesized by conventional vessel process are shown in *Figure 2.* In spite of the data scattering, connected mainly with adjustments in synthesis conditions for any single product, the degree of *LCB* is practically the same over the whole range of molecular weights, independent of the product examined.

Such a result seems surprising when it is considered that it was obtained on a quite large *MFR* range and under synthesis conditions covering practically the whole range of commercial products.

Should these findings be confirmed for a larger number of samples then by defining a single correlation [η]–*M*, we will arrive at a routine evaluation for the true molecular weight of all these polymers by the g.p.c. universal calibration method[23–25].

Unlike samples obtained by the tubular process, those obtained by the vessel method show no simple and immediate correlation between *LCB* and the other parameters (A_2, R_g). The reason is both their intrinsic variability and other factors, probably connected with the synthesis conditions which cannot be isolated.

From comparison of the data in *Tables 2* and *3* and *Figures 1* and *2*, all polymers obtained by the conventional vessel process show a higher *LCB* than those produced by the conventional tubular method and the difference gradually increases with increasing the *MW.* This is also proved indirectly by the *MWD,* which is larger in the former samples than in the latter.

Figure 3 shows the results obtained from the structural characterization of LDPE samples produced by a modified vessel process enabling synthesis under better conditions.

The results obtained lead to the conclusion that even for the vessel process – though to a lesser extent than for the tubular one – technological process modifications (i.e. increase in the number of zones) definitively allow the reduction of *LCB.* In this case too a sharpening of *MWD* is observed on decreasing *LCB*: this agrees not only qualitatively with what occurs in the samples prepared by the tubular process.

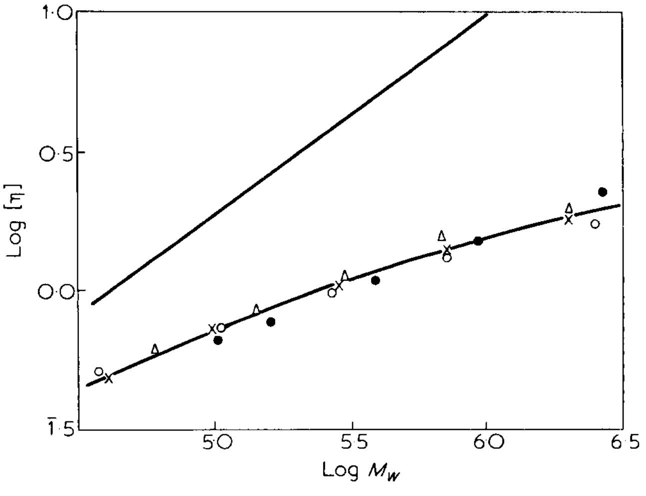

Figure 2 Comparison among the relationships log [η]-log M_w of LDPE samples by vessel processes (○, *V*-1; X, *V*-2; △, *V*-3; ●, *V*-4)

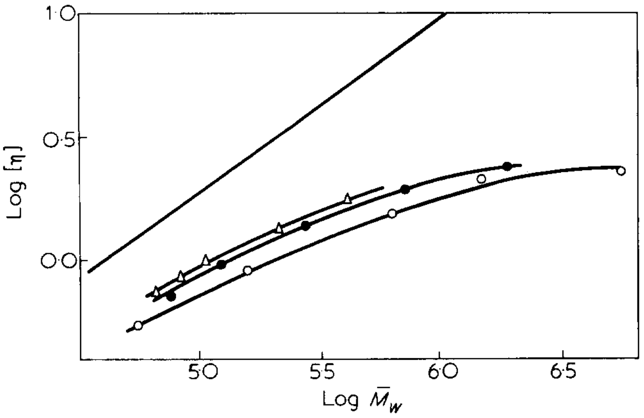

Figure 3 Comparison among the relationships log [$\bar{\eta}$] -log M_w of LDPE samples by modified vessel process (△, *VM*-1; ●, *VM*-3; ○, *VM*-5

The plots which may easily be obtained from the previous curves ($g = f(M)$, $\lambda = f(M)$, etc.), are not reported here because of both typographical reasons and because they do not give any essential contribution to the discussion.

From the results obtained it is possible to draw some reasonable conclusions about the influence of the processes and their modifications on the *LCB* of samples without considering possible structural differences occurring between them. Sure conclusions cannot be drawn from the data available from a structural investigation, even if some discrepancies might be interpreted as an indication of a different type of *LCB*.

CONCLUSIONS

The results on LDPE obtained lead to the following conclusions: the degree of *LCB* increases with the molecular weight according to a non-linear relationship; the degree of *LCB* depends on the type of process (vessel or tubular) adopted for the synthesis and, in the case of conventional technologies, it is higher with the vessel process; the degree of *LCB* and its dependence on molecular weight (for the conventional vessel process) is almost the same for all examined products, independently of the type of application they were intended for (*MFR* 1 ÷ 80); the degree of *LCB* may be considerably reduced by suitable modifications of the two processes.

While the first conclusion is obvious and is in agreement with the data reported in the literature, the others seem to give a new and fundamental contribution to the knowledge of the material and processes adopted for its synthesis. The above statements will be proved, and a more complete understanding will be acquired, by rheological investigations on the raw samples and fractions, which will be dealt with in subsequent papers.

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