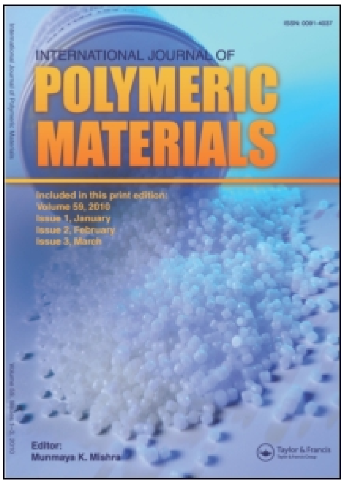

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Structure-Property Relationships in Low-Density Polyethylene

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Structure—Property Relationships in Low-Density Polyethylene

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Modern techniques were adopted and utilized for molecular-weight characterization of commercial low-density (branched) polyethylenes. The index of long-chain branching was uniquely related to that of molecular-weight dispersion, D_n. Two groups of low-density polyethylenes were visualized, differing in width of MW distribution and in the branching index. An attempt was made to relate the flow properties, melt-flow index (MFI) and intrinsic viscosity $[\eta]$, as well as some physical properties—density, tensile strength, ultimate elongation and resistance to environmental stress cracking—to a typical molecular parameter. In all correlations, the two groups are represented by two distinctly different curves. By combining the parameter g for long-chain branching with the weight average molecular weight, $\bar{M}_w$, the flow parameters are unified into single curves. The mechanical properties studied were found to improve increasing $\bar{M}_w$ and with narrowing of the molecular-weight distribution.

INTRODUCTION

Previous publications[1–3] dealt with the molecular-weight distribution (MWD) and degree of long-chain branching (LCB) of commercial low-density polyethylene (LDPE) samples. The GPC apparatus used for this characterization study provided a crude chromatogram based on elution volume. Conversion of the latter to molecular-dimensions of the branched chains was effected through the concept of the "universal calibration",[4] wherein the product of molecular-weight and intrinsic viscosity, $M \cdot [\eta]$, represents the hydrodynamic volume of any polymer, whether linear or branched. The final MWD curve was calculated by two alternative approaches.

The first approach[1] postulates that, for each polymer sample, the frequency of long branches (α) is constant above some critical molecular weight, M_0.

The branching index, n (number of long-chain branches per unit molecular weight) is given by:

$$n = a(M - M_o) \quad \text{for } M \geq M_o \tag{1}$$

At the same time, n is also (indirectly) related to the intrinsic viscosity through the familiar branching parameter, g, which describes the relative reduction in typical chain length $(\overline{s^2})^{\frac{1}{2}}$ (radius of gyration) when linear chains (l) are replaced by branched ones (b) at the same molecular weight:

$$g = \frac{\overline{s_b{}^2}}{\overline{s_l{}^2}} < 1 \tag{2}$$

The relation between g and n was determined by Zimm and Stockmayer[5]; g can also be estimated by the intrinsic viscosity ratio[6]

$$g^{\frac{1}{2}} = \frac{[\eta]_b}{[\eta]_l} \tag{3}$$

After iterative trial and error calculations (aided by a digital computer) the following data were compiled for each polymer sample: the complete MWD curve, the parameter g and index n_w (weight-averaged), various molecular-weight averages, and finally distribution indices, of which the "dispersion index" D_n is mostly recognized as representative of the width of the distribution.

$$D_n = \overline{M}_w/\overline{M}_n \tag{4}$$

The second approach[2] dispenses with the branching indices, and the effect of LCB on the intrinsic viscosity is indirectly expressed by a polynomial, namely:

$$\log[\eta]_b = \log K + a\log(M) + b\log^2(M) + c\log^3(M); \text{ for } M \geq M_o \tag{5}$$

$$\log[\eta]_b = \log[\eta]_l = \log K + a\log(M); \text{ for } M < M_o \tag{6}$$

The appropriate value for M_o is around 6,000–12,000.

The resultant averages $\overline{M}_w$ and $\overline{M}_n$ obtained by both methods agreed reasonably well with directly observed data obtained by light scattering and cryoscopy by F. W. Billmeyer, Jr.

In this work, the first approach was used for exact characterization of local commercial LDPE samples, with the calculated molecular weight averages and the indices for LCB and MWD related to gross flow indices and physical properties.

RESULTS AND DISCUSSION

Eight samples of low-density polyethylene (the I.C.I. autoclave process) were provided by courtesy of the Israel Petrochemical Enterprises Ltd., Haifa. These samples fall into two distinct groups of different sets of polymerization conditions, group 1 (grades A, B, C and D) being relatively narrower-distributed and less long-chain branched than group 2 (grades E, F, G and H). The major data of their characterization, as interpreted from GPC measurements are shown in Table 1, together with previously published data for three samples communicated by F. W. Billmeyer, Jr. (group 3 in the table). Physical properties, listed in Table 2, include average values of density, tensile strength, ultimate elongation and resistance to environmental stress cracking (ESC), all measured by ASTM methods [D-1693 for ESC resistance (bent-strip test), D-638 for tensile strength], and representing the most reliable statistical data for these polymer grades.

TABLE I

Characterization parameters of LDPE samples

Polymer		$\bar{M}_n$	$\bar{M}_w$	$\alpha \cdot 10^4$ LCB Frequency	n_w LCB index	g	D_n Dispersion index	MFI	130°C $[\eta]$ TCB
Group	Grade								
1	A	21,000	320,000	1.80	57.8	0.1483	15.24	0.25	1.160
	B	24,400	191,000	2.40	45.8	0.1727	7.83	0.67	0.965
	C	23,000	140,000	3.86	53.8	0.1560	6.09	2.00	0.766
	D	18,000	77,600	5.69	44.1	0.1745	4.31	23.80	0.560
2	E	21,100	691,000	4.23	293.3	0.0450	32.80	2.00	0.975
	F	18,600	620,000	5.83	361.6	0.0382	33.33	7.30	0.860
	G	15,700	518,000	7.62	394.9	0.0356	32.90	18.80	0.730
	H	15,600	470,000	9.71	456.9	0.0318	30.10	34.00	0.635
3	75	14,100	427,000	5.38	229.0	0.0545	30.30	1.80	0.800
	76	15,100	239,000	4.61	110.0	0.0941	15.80	1.95	0.730
	77	19,800	458,000	3.25	148.0	0.0757	23.00	0.16	0.985

The indices for LCB (n_w) and MWD (D_n) were found to be inter-related, as shown by the single straight line in Figure 1, in which data on group 3 as well as those of other workers[7] were successfully incorporated. Apparently, in commercial LDPE both long-chain branching and MWD width are affected by the same reaction conditions.

The flow parameter most useful in industry is known as the melt-flow index (MFI), which has been previously related to the MW of linear polyethylene.[8] In spite of its ambiguous rheological meaning, it is no doubt a sensitive and rapid parameter for the process control.[9] The dependence of MFI on $\bar{M}_w$ is

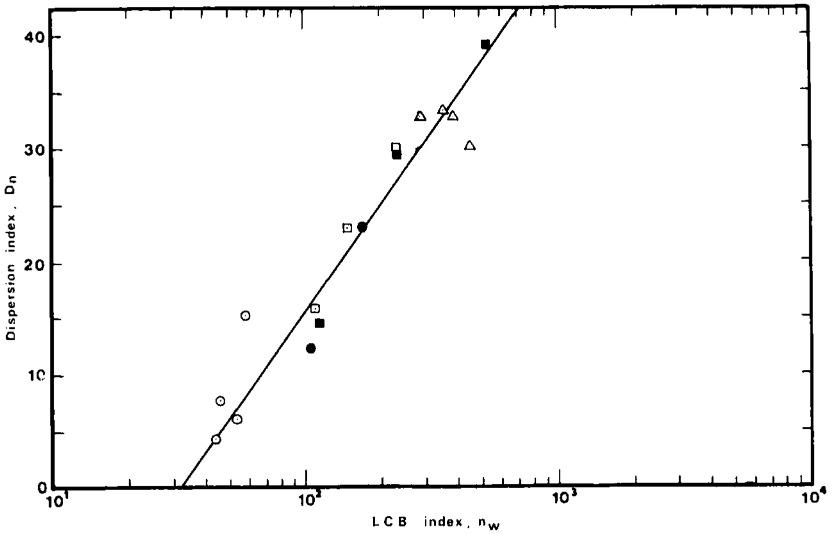

FIGURE 1 Correlation between branching index, n_w, and MW dispersion index, D_n. (○) group 1; (△) group 2; (□) group 3; (■) data from ref. 7; (●) experimental polymers.

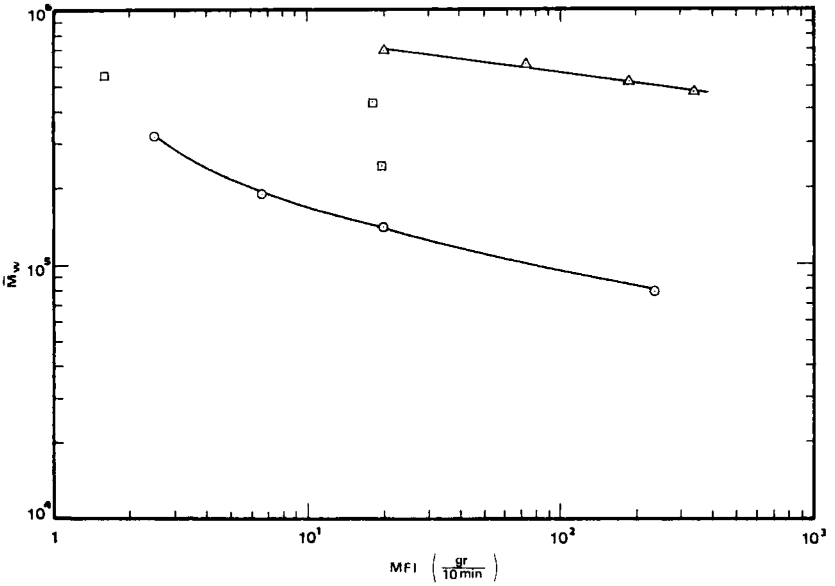

FIGURE 2 Melt flow index—$\bar{M}_w$ relationship. (○) group 1; (△) group 2; (□) group 3.

shown in Figure 2. Groups 1 and 2 are represented here by two distinct curves, but if $\overline{M}_w$ is replaced by the product g · $\overline{M}_w$, all samples (including group 3) fall roughly on a single straight line (in log–log coordinates) with slope—1/4.5 (Figure 3). This single line is in agreement with the equation for low-shear melt viscosity of branched polymers,[10]

$$\eta_o = K(g\,M_w)^b. \tag{7}$$

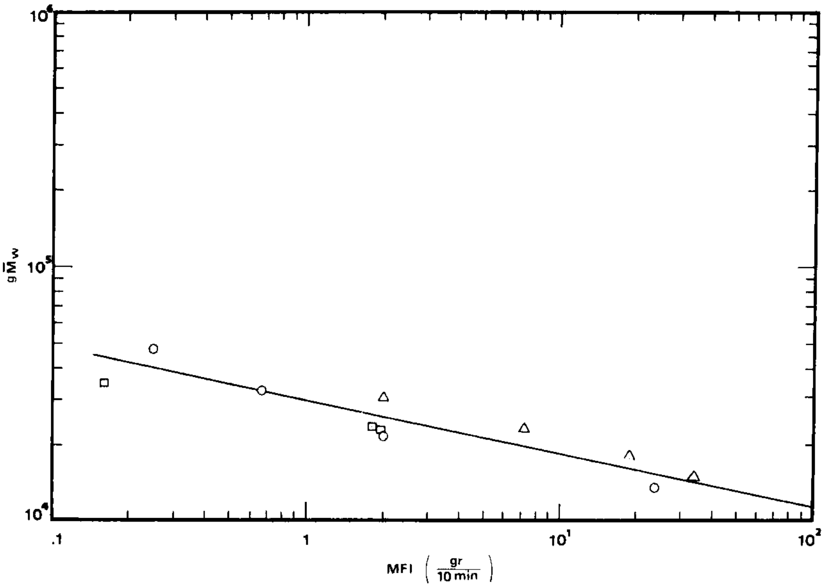

FIGURE 3 MFI—g · $\overline{M}_w$ relationship.
(○) group 1; (△) group 2; (□) group 3.

Experimental values of the exponent b for LDPE are known to lie in the range 3.5÷6.5. It is worthwhile stressing that high values of MFI do not necessarily entail a low molecular weight (as shown in Table 1) considering the high sensitivity of melt-flow properties to changes in LCB and MWD. It is also to be stressed that group 2 verifies higher values for $\overline{M}_w$ due, partially, to the appearance of LCB.

Another useful characterization parameter is the intrinsic viscosity. In Figure 4, groups 1 and 2 are again represented by two distinct curves (decreasing curvature with increasing molecular weight is typical of branched polymers,[2]) but when $[\eta]$ is replaced by $[\eta]/g^{0.5}$, all polymers again fall on a single straight line (slope 0.6 in log–log coordinates). This is actually based on Eq. (3), in this case for whole polymers, and shown in Figure 5.

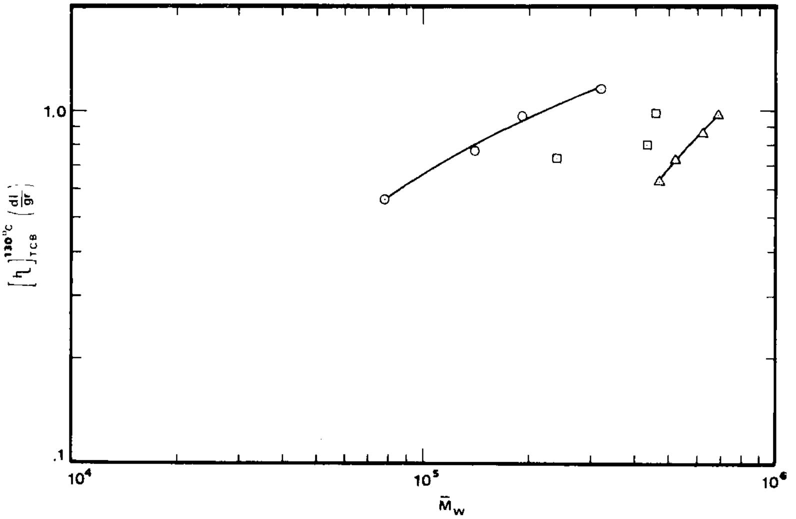

FIGURE 4 Intrinsic viscosity—$\bar{M}_w$ relationship.
(○) group 1; (△) group 2; (□) group 3.

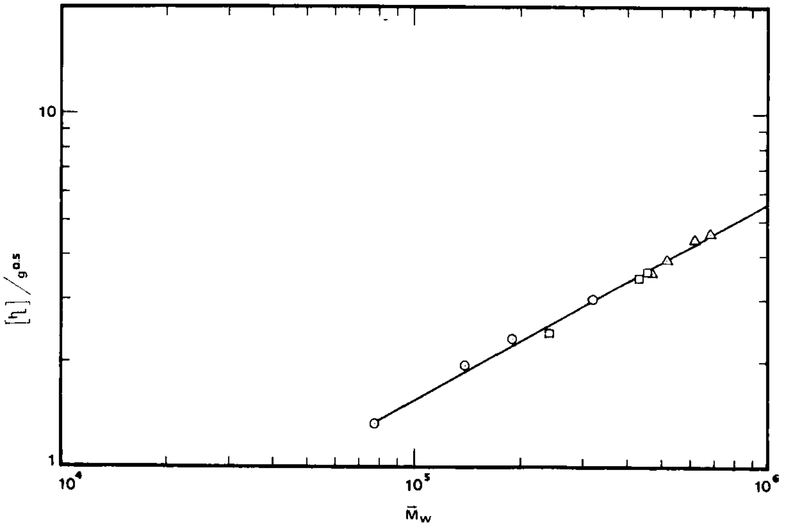

FIGURE 5 $[\eta]/g^{0.5}$—$\bar{M}_w$ relationship.
(○) group 1; (△) group 2; (□) group 3.

The conclusion is that both MFI and $[\eta]$ can be uniquely related to $\bar{M}_w$, once the degree of long-chain branching has been taken into account. The frequencies of LCB were found to decrease with increasing $\bar{M}_w$, as shown by the two curves in Figure 6.

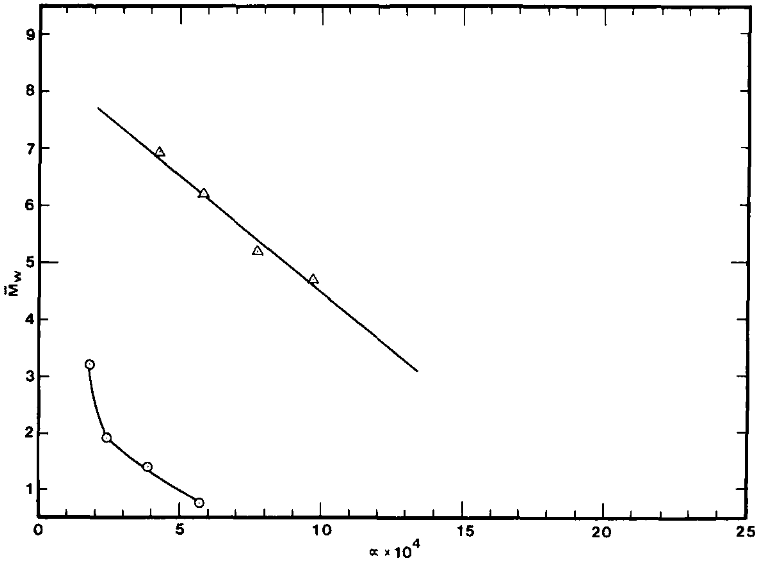

FIGURE 6 Dependence of LCB frequency, α, on $\bar{M}_w$. (○) group 1; (△) group 2.

Extreme caution is called for in interpreting data on mechanical properties, in view of their sensitivity to pretest conditioning with its effect on the morphology of the solid (degree of crystallinity, size and shape of spherulites, etc.). Taking the manufacturer's data, the ultimate elongation was found to increase with the weight-average molecular weight, $\bar{M}_w$ in each group separately (Figure 7), (although no single correlation could be found with other MW averages or with the various MWD indices) and the same pattern was observed for ESC resistance (Figure 8). The two figures indicate that group 1, which is narrower-distributed, has better mechanical properties than group 2 with its wide distribution and high degree of LCB; on the other hand, group 2 shows better flow properties (higher melt-flow index). The whole pattern of flow properties, over a wide range of shear-stresses, is now in the process of evaluation.

The notion that physical properties (such as tensile strength, ultimate elongation, impact strength and ESC resistance) are improved by increasing

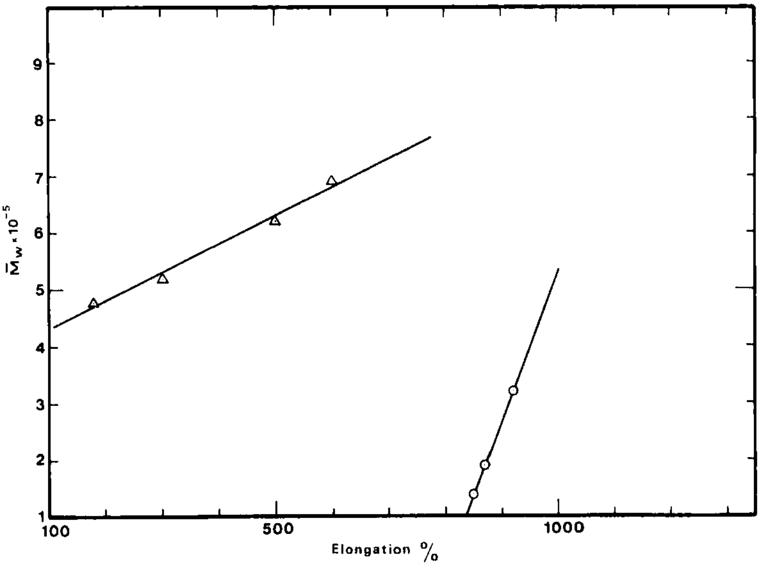

FIGURE 7 Dependence of ultimate elongation on $\bar{M}_w$.
(○) group 1; (△) group 2.

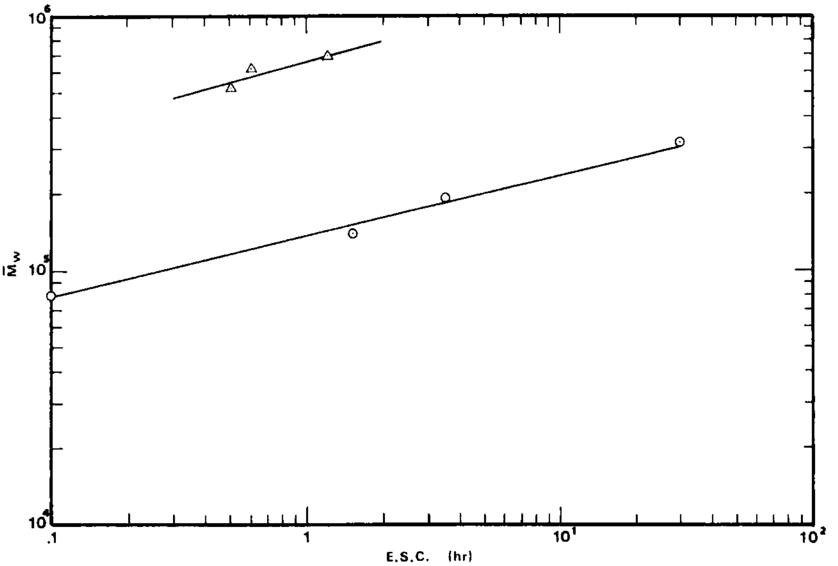

FIGURE 8 Dependence of resistance to ESC on $\bar{M}_w$.
(⊙) group 1; (△) group 2.

the molecular weight and narrowing its distribution has been mentioned by various authors,[11–13] some preferring $\overline{M}_n$ to $\overline{M}_w$ for their correlations.[14]

Table 2 includes also the densities of the polymer samples, which are seen to decrease monotonically with increasing n_w (especially in group 2)—indicating that the degree of short-chain branching (controlling density) has the same variation pattern as LCB. The tensile strength in each group seems to increase with both $\overline{M}_w$ and density. Data on impact strength are not reported, but some limited information showed a definite increase with $\overline{M}_w$.

TABLE II

Physical properties of LDPE samples

Polymer		MFI	$\bar{M}_w$	Density	Tensile strength	Elongation	ESC
Group	Grade			gr/cm³	kg/cm²	%	(hr)
1	A	0.25	320,000	0.923	155	920	30.0
	B	0.67	191,000	0.923	154	870	3.5
	C	2.0	140,000	0.921	135	850	0.5
	D	23.8	77,600	0.921	120	—	0.1
2	E	2.0	691,000	0.919	130	600	1.2
	F	7.3	620,000	0.918	110	500	0.6
	G	18.8	518,000	0.916	100	300	0.5
	H	34.0	470,000	0.915	86	180	—

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