

Distribution of Molecular Weights and Branching of High-Density Polyethylene

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Synopsis

Samples of industrial high-density polyethylenes (Liten Macro, Liten FB 29, and Hostalen GM 9255 F) were divided into fractions by precipitation fractionation. The original samples and their fractions were characterized by light scattering, GPC, and viscometry. For all samples the molecular weight distribution is of logarithmic-normal type. High-density polyethylenes under investigation contain also high-molecular-weight fractions of pronouncedly branched structure, the content of branched molecules being, of course, considerably smaller than that in low-density polyethylenes.

INTRODUCTION

Knowledge of the molecular structure of polyethylene (PE) is necessary for understanding the properties of this polymer, both at the molecular level and with respect to processing and application.¹⁻³ In the first approximation properties of the individual macromolecules depend on their molecular weight and structure (here, e.g., chain branching). Similarly, for a polymer which is an assembly of macromolecules, its properties depend on the distribution of molecular weights (MWD) and structures; the two distributions may be interdependent. A polymer is well characterized, if these distributions are known; in practice, however, one mostly has to content oneself with more modest information, e.g., with the knowledge of moments of the distribution functions—number, weight, and sometimes z -average molecular weight—and with variously defined parameters of branching.

The most extensive information on a PE sample may be obtained by its fractionation followed by the characterization of fractions. Fractionation may be carried out using differences in the phase separation behavior of macromolecules differing in molecular weight and structure (precipitation fractionation or fractional dissolution), their different ability to crystallize from solution (fractional crystallization), or the polymer can be fractionated chromatographically or by other methods. The fractionated polymer is then analyzed after isolation of the individual fractions or continuously. Methods fractionating the polymer either according to molecular weight or to the degree of branching would be de-

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sirable; in practice, however, fractionation is always affected by both factors, although to a different extent.

In particular light scattering, gel permeation chromatography (GPC), osmometry, and viscometry are used for the molecular characterization of PE, though some other methods may also be employed (e.g., sedimentation analysis, NMR, and the like).

Of some recent methods utilized in the description of the molecular structure of PE, that combining a gel permeation chromatograph (separation method) with a detector based on measurement of the intensity of scattered light⁴ (analytical method) may be mentioned. Another interesting approach is the "cross fractionation"⁵ consisting in a gradual dissolution of PE with increasing temperature (the fractionation method based on differences in the ability of variously branched macromolecules to crystallize) with subsequent characterization of the eluent by GPC (used in this case as a combination of fractionation and analytical method).

Isolation of PE fractions followed by their analysis is more common, though at the same time more labor-consuming. The best fractions with a relatively narrow MWD may be obtained by preparative GPC.^{6,7} However, satisfactory results may also be achieved by other carefully performed fractionation procedures (e.g., by precipitation fractionation).

In this study, light scattering^{8,9} and viscometry¹⁰ were used along with GPC for the description of PE fractions prepared by precipitation fractionation. The aim consisted of comparing the MWD and the extent of branching for three industrial samples of high-density polyethylene of various molecular weights, prepared by different technologies.

EXPERIMENTAL

Polymers

The following industrial high-density polyethylene (HDPE) samples were used in the investigation of molecular weight distribution and branching:

(a) Liten Macro, a reference sample already investigated in greater detail,⁹ whose further characterization was regarded as desirable; according to the producer's data (Chemopetrol, ČSSP Chemical Works, Litvínov, Czechoslovakia), it is an injection-molding type of linear PE, Liten MB 62, with a narrow MWD.

(b) Liten FB 29, a foil type of HDPE of the same origin, containing a small quantity of butene comonomer; this is a polymer with broad MWD. Both polymers are manufactured with the Union Carbide type catalytic system.

(c) Hostalen GM 9255 F, a foil type of linear HDPE produced with Ziegler catalytic system and distributed by Hoechst AG, West Germany.

The samples were chosen so as to comprise the largest possible range of molecular weights.

Fractionation

The solvent system used in precipitation fractionation consisted of commercial reagent grade quality xylene and ethylcellosolve (ECS, 2-ethoxyethanol). The

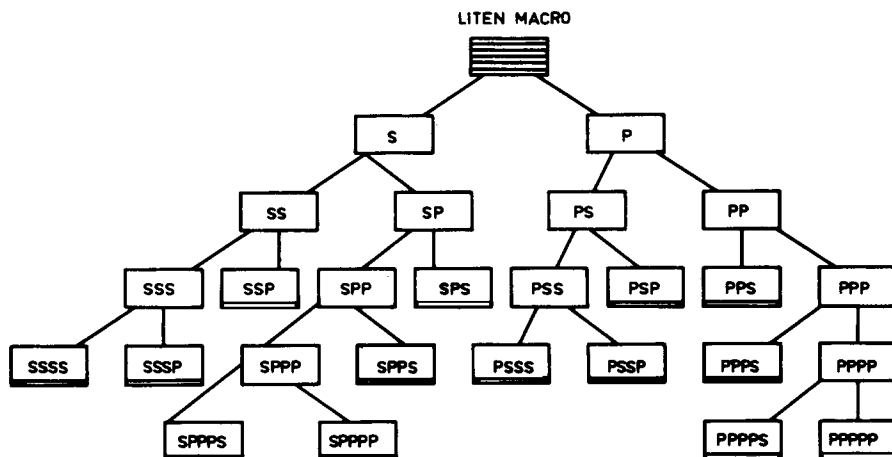


Fig. 1. Fractionation scheme of Liten Macro.

system was chosen because of the approximately identical boiling point of both components (137–138°C). Its use has also been often reported in the literature.^{11–15}

Some 20-g PE granules dissolved in xylene at 128°C (0.1 wt % of stabilizer Irganox 1010) were introduced into a 2-L fractionation flask. After that, ECS was added until a slight but constant turbidity appeared, the temperature was raised until the solution became clear and then decreased again to the original value. The system was left at rest until phase separation was reached (8–24 h). The whole system was kept under a slight overpressure of nitrogen in order to avoid oxidative processes during long-term heating. The diluted (lower) phase was pumped over into the other vessel, the polymer rich (upper) phase was dissolved in xylene, and the fractionation was repeated until polymer fractions weighing less than about 2 g were obtained.

From here onwards, the polymer present in the more concentrated phase is referred to as the P (precipitated) fraction, and that from the dilute phase is denoted as the S (soluble) fraction. If the resulting fraction is denoted as, e.g., SSP it means that the fraction was isolated after threefold phase separation, when in the first and second separation the dilute (S) phase was each time separated and subjected to further treatment, while in the third phase separation it was the concentrated phase (P). An example of a fractionation scheme is given in Figure 1.

The fractions were isolated by precipitating the polymer into excess of methanol; the concentrated phase was diluted with xylene prior to the precipitation. The fine polymeric precipitate was decanted with methanol, quantitatively separated by filtration and dried at 60°C *in vacuo*. The sum of weights of the fractions was 96–101 wt % of the original polymers.

Light Scattering and Viscometry

All light scattering measurements were carried out in diphenylmethane at 142°C (θ -solvent for PE¹⁶) with a FICA 50 apparatus in the unpolarized primary beam of the wavelength 546 nm. The refractive index increment^{8,9} was taken

as $-0.125 \text{ cm}^3/\text{g}$. More detailed data on the light scattering technique are given elsewhere.⁹

The intrinsic viscosities were determined in 1,2,4-trichlorobenzene at 130°C by a method described earlier.¹⁰

Gel Permeation Chromatography

The GPC analyses were performed with a Waters GPC Model 200 apparatus at 135°C with *o*-dichlorobenzene as solvent. A system of columns packed with Styragel was calibrated with polystyrene standards (M_w up to 2.7×10^6) having a narrow MWD and supplied by Waters. The samples were injected as 1/16% (w/w) solutions. The average molecular weights of PE samples were calculated using the Benoît universal calibration and constants of the Mark-Houwink equation reported by Ogawa and Inaba.¹⁷ In the analysis of a standard HDPE sample (SRM 1475), these constants provided good agreement with data reported by the (U.S.) National Bureau of Standards.¹⁸ The results were corrected for sample spreading in the column by means of a simple method suggested by Hamielec and Ray.¹⁹ Hydrodynamic volumes of all PE fractions were within the range of the universal calibration dependence.

RESULTS AND DISCUSSION

Molecular Weight Distribution

In the characterization of fractions by light scattering, difficulties arose in the case of fractions which in the last step were isolated from the dilute phase (the last letter in the designation of the fractions is S). Virtually all fractions of this type contained a small amount of high-molecular-weight particles which was reflected in a curvature of the radiation envelopes of scattered light in the range of low angles. This effect was most pronounced for samples with low molecular weight. The molecular weight determination of fractions where isolation from the concentrated phase was the last step did not involve any difficulties. For this reason, we attempted to minimize the number of fractions of the type S by adjusting the fractionation scheme. Furthermore, most fractions of this type were formally transformed into fractions of the type P by dissolving them in a small amount of xylene and adding ECS in large excess. The fractions thus adjusted could be characterized by light scattering without difficulty.

The results of fractionation of all three PE samples have been summarized in Table I. The following calculation of the MWD was based on the weight-average molecular weights M_w obtained by light scattering, because the M_w values obtained from GPC may be affected by branching. The data concerning the width of MWD, viz., the polydispersity index M_w/M_n , may also be affected by branching, but to a much smaller extent,²⁰ and the potential effect of branching on this index was therefore ignored. Summarily, the discussion of the results may be presented in the following points:

(1) The MWD of polyethylene often satisfies the logarithmic-normal (Wes-slau) distribution²¹

$$w(M) = \frac{1}{\beta\sqrt{2\pi M}} \exp\left[-\frac{1}{2\beta^2} \log^2\left(\frac{M}{M_0}\right)\right] \quad (1)$$

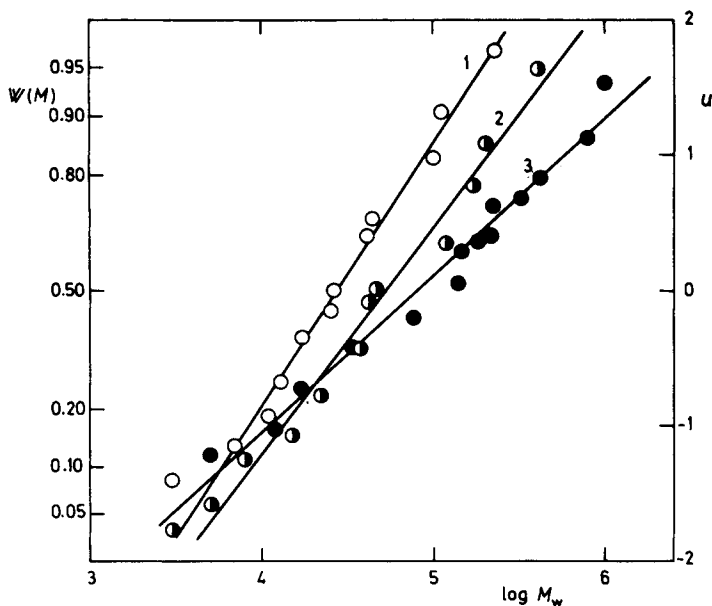


Fig. 2. Wesslau's test for the applicability of the logarithmic-normal molecular weight distribution. $W(M)$ is the integral MWD function, u is the parameter of the integral distribution function $F(u)$ of normal distribution $N(0,1)$. Fractions of Liten Macro (○), Liten FB 29 (◐), and Hostalen GM 9255 F (●).

with the parameters β and M_0 related to the average molecular weight values M_w and M_n by

$$\begin{aligned} M_w &= M_0 \exp(\beta^2/2) \\ M_n &= M_0 \exp(-\beta^2/2) \end{aligned} \quad (2)$$

If the molecular weight of PE chains obeys this distribution the logarithm of molecular weight has a normal (Gaussian) distribution. The Wesslau plot²¹ of the integral MWD function $W(M)$, as a function of the logarithm of molecular weight, is then linear. In such a plot the scale on the y-axis is nonlinear and determined by the tabulated integral distribution function of the normal (Gaussian) distribution, $F(u)$, of the parameter u . For all the three PE samples the dependences of the Wesslau plot may be regarded as linear within the limits of experimental error (Fig. 2). Hence, the weight MWD functions of the samples under investigation may be considered to be logarithmic-normal.²¹

(2) The width of MWD of the samples under investigation increases somewhat with increasing average molecular weight M_w (Fig. 2), but this finding cannot be regarded as generally valid.

(3) Molecular weight of the polymer obtained as a weighed sum of molecular weights of the individual fractions is lower in all three cases than that of the unfractionated sample: for Liten Macro by 11%, for Liten FB 29 by 38%, and for Hostalen GM 9255 F by 45%. The intrinsic viscosity calculated similarly from fractionation data is also lower compared with that of the initial samples, by 7%, 10%, and 14%, respectively. This fact is reflected in a displacement of the MWD determined from fractionation data [Fig. 3(—)] toward lower molecular weights compared with the MWD calculated for the unfractionated polymer (---) from

TABLE I
 Characteristics of Polyethylene Samples and Their Fractions Determined by Light Scattering (LS) and Gel Permeation Chromatography (GPC), and
 Viscometrically (V)^a

No.	Polymer/fraction Type	w_i	$10^{-3} M_w$		M_w/M_n GPC ^c	$[\eta]$ V ^d	ξ_7 V
			LS ^b	GPC ^c			
Unfractionated samples							
	Liten Macro		87	88	7.7	1.08	0.88
	Liten FB 29		220	165	14.1	1.39	0.62
	Hostalen GM 9255 F		540	250	11.8	1.59	0.36
LITEN Macro							
1	SSSS	0.0813	(3) ^e	2.2	1.47	0.125	1.00
2	SSSP	0.0456	(7)	4.9	1.14	0.239	1.00
3	SSP	0.0488	(11)	8.2	1.22	0.322	0.98
4	PSSS	0.0415	13	13	2.29	0.351	1.01
5	SPS	0.1420	17	16	1.41	0.442	1.00
6	SPPS	0.0803	25	20	1.39	0.603	1.03
7	SPPPS	0.0595	26	27	1.42	0.654	1.09
8	SPPPP	0.1587	41	47	1.33	0.800	0.95
9	PSSP	0.0422	45	44	1.33	0.927	1.03
10	PPPS + PSP	0.1351	99	92	1.38	1.58	0.99
11	PPS	0.0718	110	115	1.44	1.40	0.83
12	PPPPS	0.0555	230	230	1.42	2.60	0.89
13	PPPPP	0.0377	570	590	1.74	4.62	0.84
LITEN FB 29							
1	SSSSSS	0.0379	(3) ^e	1.9	1.41	0.108	0.86
2	SSSSSP	0.0214	(5)	5.0	1.25	—	—
3	SSSSP	0.0483	(8)	7.5	1.29	0.284	1.10
4	SSSP	0.0354	15	12	1.26	—	—
5	SSP	0.0721	22	19	1.24	0.540	1.00
6	SP	0.1183	37	29	1.65	0.728	0.95

7	PSSS	0.1382	43	42	2.33	0.800	0.97
8	PPSS	0.0308	45	42	1.54	0.858	0.97
9	PSSP	0.1325	120	110	1.45	1.51	0.80
10	PSP	0.1475	175	140	2.11	1.67	0.73
11	PPSP	0.0763	190	170	1.48	1.81	0.72
12	PPPS	0.0894	430	430	3.10	2.88	0.70
13	PPPPP	0.0519	570	610	2.04	2.52	0.46
HOSTALEN GM 9255 F							
1	SSSSSS	0.1125	(5) ^e	3.2	1.78	0.182	0.97
2	SSSSSP	0.0422	12	9.7	1.13	0.337	0.95
3	SSSSP	0.0774	17	16	1.13	0.518	1.14
4	SSSP	0.1066	33	27	1.34	0.790	1.09
5	SSP	0.0828	77	54	1.63	1.17	0.90
6	PSS	0.1002	(140)	67	6.04	1.61	0.91
7	SP	0.0928	145	72	1.76	1.50	0.73
8	PPSSS	0.0256	180	80	3.22	—	—
9	PPPS	0.0220	(215)	130	2.38	—	—
10	PSP	0.0692	220	160	2.26	1.65	0.61
11	PPPPS	0.0164	330	165	2.08	2.41	0.66
12	PPSSP	0.0466	430	240	1.65	2.64	0.58
13	PPPPPS	0.0734	790	360	2.13	2.41	0.35
14	PPSPS	0.0691	1000	350	2.23	2.24	0.27
15	PPSPP	0.0483	1250	640	2.69	2.19	0.23
16	PPPPPP	0.0149	1380	620	3.07	2.96	0.30

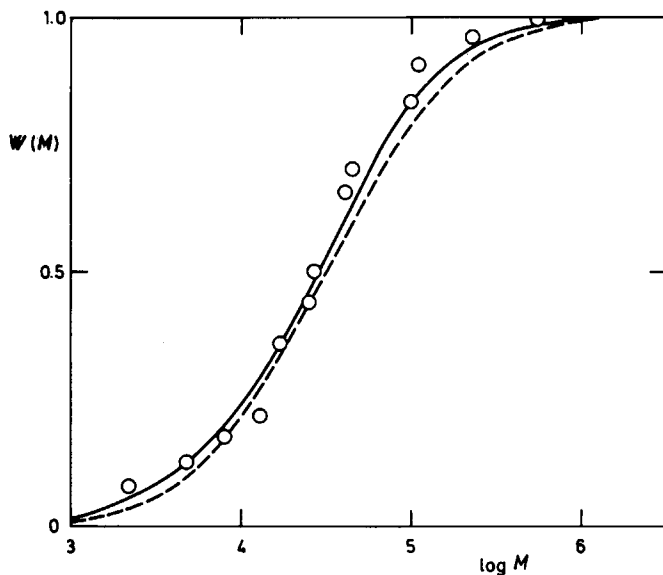
^a w_i is the weight fraction of the i th fraction, M_w and M_n are the weight- and number-average molecular weights, respectively, $[\eta]$ is the intrinsic viscosity (dL/g), and g_η is the branching index defined by eq. (3).

^b Diphenylmethane, 142°C.

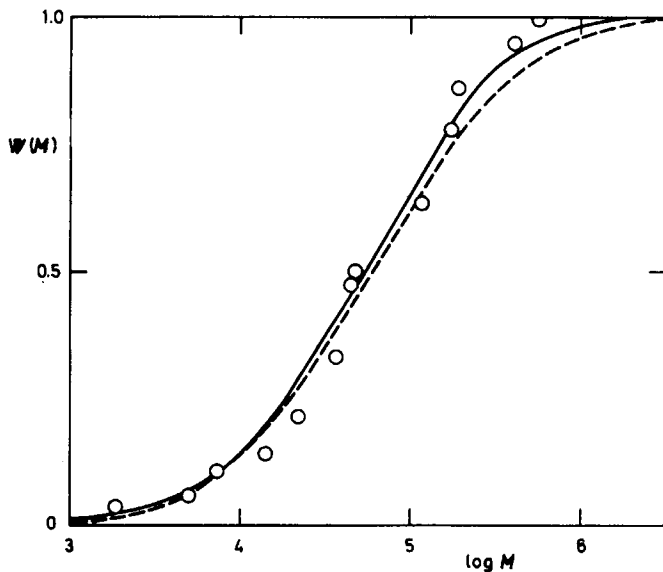
^c *o*-Dichlorobenzene, 135°C.

^d 1,2,4-Trichlorobenzene, 130°C.

^e The results in parentheses are less accurate.



(a)



(b)

Fig. 3. Integral weight distribution function $W(M)$ of molecular weights M of PE samples under investigation: (a) Liten Macro, (b) Liten FB 29, and (c) Hostalen GM 9255 F. (---) Logarithmic-normal MWD of the unfractionated polymer: The distribution parameters were determined from molecular weights M_w obtained by light scattering and from the polydispersity index M_w/M_n obtained by GPC. (—) MWD derived from the weighed sum of distribution functions of the individual fractions: The MWD is assumed to be logarithmic-normal also for the fractions. The parameters of these distributions were calculated from the known molecular weight M_w obtained by light scattering and from the polydispersity index M_w/M_n of the individual fractions determined by GPC. The points correspond to the individual fractions; the coordinate $W(M_i) = \sum w_i$ is the sum of weight fractions of the i th fraction and of all fractions with lower molecular weight.

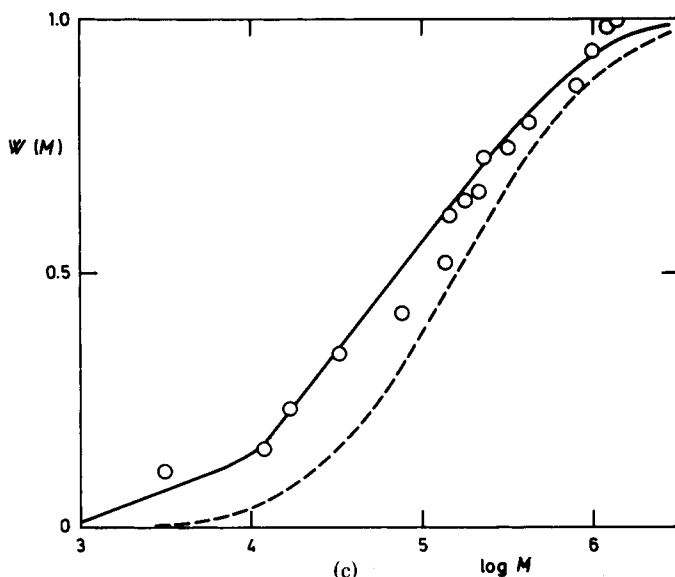


Fig. 3 (Continued from the previous page.)

M_w and M_n , assuming the Wesslau distribution. In particular, the high-molecular-weight parts of the curves are displaced with respect to each other. Differences in the low-molecular-weight parts of integral distribution functions are probably due to a considerable experimental error involved in the molecular weight determination of low-molecular-weight fractions. The contribution of these fractions to the weighed sum which determines the overall weight-average molecular weight is small and the calculated molecular weight value M_w is only little affected by them. The likely explanation is that during the fractionation PE undergoes partial degradation in spite of measures which should impede it (presence of antioxidant, inert atmosphere). This is also indicated by the greater decrease in molecular weight of samples with higher molecular weight. Imperfect drying of fractions which would be reflected similarly does not seem likely.

(4) With most high-molecular-weight fractions, a discrepancy has been observed between the molecular weight M_w determined by light scattering and by GPC; values provided by the latter were systematically lower, especially for Hostalen GM 9255 F. This could be explained by, e.g., the presence of microgel in the fractions, which would considerably affect M_w determined by light scattering in the direction of higher values, while the GPC results in the presence of the microgel would remain virtually unaffected. The scattering data (Fig. 4), however, do not suggest the presence of the microgel in the absolute majority of cases (cf. also the discussion of the problem of S fractions). This is why we adopted a view that the high-molecular PE fractions are partly branched, although this possibility is usually disregarded in papers with HDPE. The hypothesis has been examined in greater detail.

Branching of PE Samples

More complete and conclusive information on the branching of PE macromolecules may be obtained by the determination of intrinsic viscosity of PE

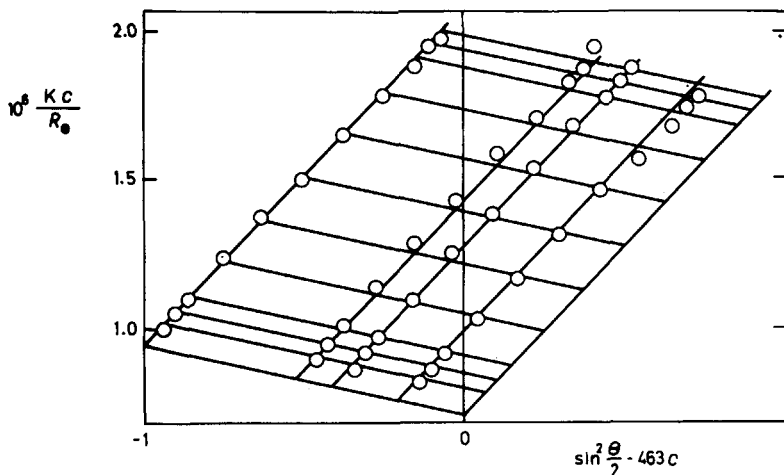


Fig. 4. The Zimm plot for the fraction PPPPP of Hostalen GM 9255 F; diphenylmethane, 142°C.

fractions. The extent of branching can be quantitatively characterized by the ratio

$$g_{\eta} = [\eta]/[\eta]_{\text{lin}} \leq 1 \quad (3)$$

where $[\eta]$ is the intrinsic viscosity of the fraction under investigation and $[\eta]_{\text{lin}}$ is the intrinsic viscosity of linear PE of the same viscosity-average molecular weight M_v . Since the hydrodynamic volume of branched macromolecules is lower than that of linear macromolecules with the same molecular weight, the viscosity of the former is also lower than the intrinsic viscosity of the corresponding linear sample.

For linear PE, Wagner and Hoeve²² give a relation between the intrinsic viscosity determined in 1,2,4-trichlorobenzene at 130°C and the viscosity average molecular weight as

$$[\eta]_{\text{lin}} = KM_v^a = 3.92 \times 10^{-4} M_v^{0.725} \text{ (dL/g)} \quad (4)$$

where K and a are constants of the Mark-Houwink equation. This relation is in good agreement with data of other authors as ensues from a comparison carried out by Scheinert.²³ On the other hand, a number of variants of this equation with different K and a values may be found in the literature, which renders the interpretation and comparison of data by various authors somewhat questionable.^{24,25}

The viscosity average molecular weights M_v were calculated from the weight-average molecular weight values M_w and from the known value of M_w/M_n using the relation²⁶

$$M_v = M_w(M_w/M_n)^{(\alpha-1)/2} \quad (5)$$

which holds for the logarithmic-normal MWD. Since the polydispersity of most fractions is relatively low, the differences between M_v and M_w are not large. In the logarithmic plot of measured intrinsic viscosity vs. the viscosity average molecular weight M_v , calculated from eq. (5), the presence of branching is reflected in a deviation of experimental data from the dependence corresponding

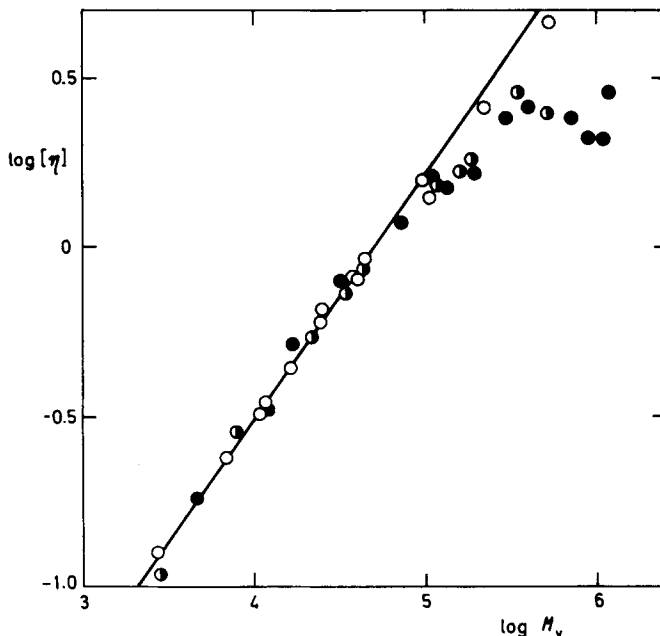


Fig. 5. Intrinsic viscosity $[\eta]$ as a function of the viscosity-average molecular weight M_v of PE fractions; 1,2,4-trichlorobenzene, 130°C: (O) Liten Macro; (◐) Liten FB 29; (●) Hostalen GM 9255 F. The straight line represents linear PE according to eq. (4).

to linear macromolecules (Fig. 5). From this figure, and from a more graphic presentation of the dependence of the branching index g_η on molecular weight (Fig. 6), the following conclusions may be drawn:

(1) Fractions of Liten Macro are virtually linear; the high-molecular-weight fractions of Liten FB29 and Hostalen GM 9255 F are partly branched.

(2) The commencing indication of branching of the latter polymers can be observed already from the molecular weight of fractions above 5×10^4 . The branching of higher-molecular-weight fractions (above about 1×10^5) cannot be neglected. The extent of branching in the range of high molecular weights is comparable with the branching observed in some cases with fractions of branched low-density PE having a comparable molecular weight²⁷ (e.g., SRM 1476), but the degree of branching of other low-density PE is much higher.^{28,29}

In the literature, the branching index g_η is often interpreted^{17,23,27,30-35} (in our view, not quite justifiably) in terms of the average number of trifunctional branching sites, n_w , in macromolecules of the given molecular weight or of branching frequency, $\lambda_w = n_w/M_w$. For the trifunctional statistical branching in a polydisperse system, Stockmayer and Zimm³⁶ have derived a relation between the number of branching sites, n_w , and the branching index g , in the implicit form

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

The index g is defined by the ratio of the mean square radius of gyration of a

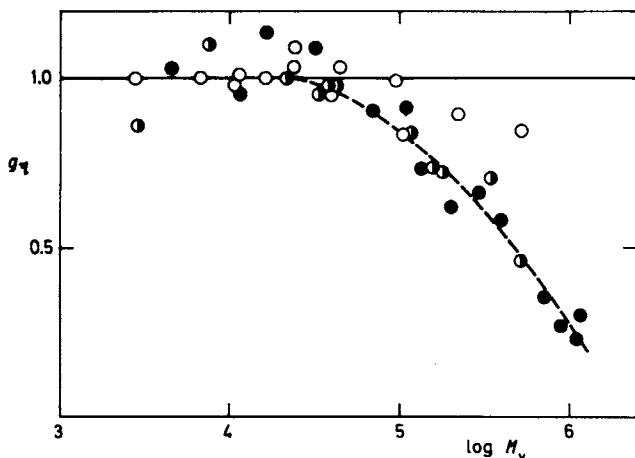


Fig. 6. The branching index g_η as a function of the viscosity-average molecular weight M_v of PE fractions. Symbols are as denoted in Figure 5.

branched macromolecule to the mean square radius of gyration of a linear macromolecule of the same molecular weight, i.e., $g = \langle r^2 \rangle / \langle r^2 \rangle_{\text{lin}}$. The relation between the g and g_η introduced by eq. (3) is given in a general form

$$g_\eta = g^\sigma \quad (7)$$

where the exponent σ varies for various models between 0.5 (starlike polymers³⁷) and 1.5 (comblike polymers³⁸). By evaluating experimental light scattering and viscometric data, Casper et al.³⁰ obtained $\sigma = 1.2 \pm 0.2$ for branched PE, even though for branched polymers of other types a lower value is usually reported (about 0.8).³⁹ For PE, also some other values of the exponent σ have been obtained,^{27,35} which, however, mostly lie in the interval determined by Casper et al.³⁰ The g index is virtually independent of the thermodynamic quality of the solvent,³³ which facilitates the application of eq. (6).

Mechanical application of eqs. (5)–(7) with $\sigma = 1.2$ to our case yields the result shown in Figure 7, which is just another qualitative presentation of data from Figures 5 and 6. Here, too, it is found that the low-molecular-weight fractions are not branched (points corresponding to linear fractions for which $n_w = 0$ are not given in Fig. 7); the number of branches in high-molecular-weight fractions increases with increasing molecular weight. On a relative scale, the extent of long-chain branching is not large compared with the usual low-density PE. In high-molecular-weight fractions there is about one branching site per 10,000 carbon atoms in the chain, while their numbers found by, e.g., NMR in LDPE are higher by at least 1 order of magnitude.⁴⁰

For some branched low-density PE the number of branching sites has sometimes been observed to be proportional to molecular weight, i.e., λ_w is constant within the limits of experimental error,^{7,14,23,41} though different for different types of PE; for other types, λ_w has been found to depend on molecular weight.^{7,14,31,33,35} Deviations in the production process of PE may markedly change the character of dependence of n_w or λ_w on molecular weight.^{29,42} Conclusions regarding the varying or constant character of these parameters modify also in those cases where the measurements are performed with the same

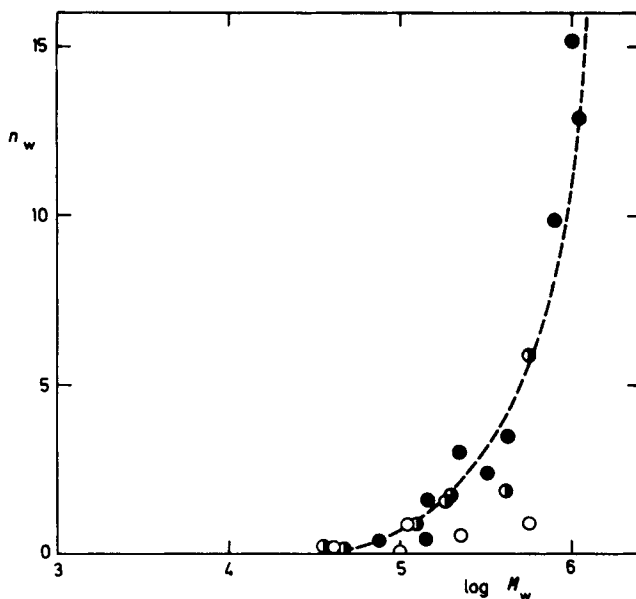


Fig. 7. Average number of branching sites in PE chains n_w as a function of the weight-average molecular weight M_w . Symbols are as denoted in Figure 5. Fractions for which $n_w = 0$ are not shown in the figure.

sample by different authors.^{28,31} The parameters λ_w calculated from our data are subjected to considerable scatter, so that no unambiguous view can be adopted in this case. It should be pointed out, moreover, that data regarding the number of long branches should be considered a mere qualitative estimate of the trend of this dependence. Models differing from those on which eqs. (6) and (7) are based give estimates of the number of long-chain branches differing by as much as an order of magnitude. Similarly, λ_w is very sensitive³⁵ to the choice of the parameter σ .

It should be noted that, due to the observed degradation of the samples during fractionation, the simultaneous involvement of branching mechanism cannot, in principle, be ruled out. Since, however, the branching indices g_n of unfractionated samples are considerably lower than unity (Table I), we conclude that the observed branching of high-molecular-weight fractions reflects and at least qualitatively characterizes the original structure of PE samples.

Thus it is very likely that also the so-called linear PE may, depending on the mode of production, contain a fraction of branched macromolecules in the high-molecular-weight region. This result is in accordance with those found by other authors.⁴³ The classification of PE as linear or branched is, in fact, based on the polymerization technology. With respect to the molecular structure of products, there is obviously a more or less continuous transition between the two limiting types.

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