Characterization of Linear Polyethylene Fractions Obtained by Preparative GPC

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Synopsis

A new preparative liquid-phase chromatograph, operating at a high temperature (160°C), allowed us to fractionate a linear polyethylene sample in narrow fractions (polydispersity about 1.1). These fractions, characterized by viscosity, light scattering, osmometry, and GPC measurements, can be used to calibrate any analytical GPC, i.e., to determine the variation of molecular weight and axial dispersion versus the elution volume.

INTRODUCTION

In a recent article,[1] we described a preparative gel permeation chromatograph and indicated its possibilities, limiting our study to polymers soluble at room temperature. Since then, we have applied this technique to the preparation of linear high-density polyethylene fractions. As is known, this polymer is soluble only at a high temperature. The preparation of such fractions seemed absolutely necessary to us in order to understand the physicochemical characteristics of this polymer and to relate them in an obvious way to its mechanical properties.

APPARATUS

The apparatus diagram is the same as the one previously described.[1] However, the difficulties arising from working at a high temperature led us to modify some of its components. The columns and the injection system are located in an oven (80 × 80 × 200 cm) whose temperature can be maintained constant up to 160°C by means of a Honeywell regulation (Versapack Type).

The fractions collector must be able to operate up to this temperature. So we built a twenty-port automatic valve whose advance is ensured by an electric motor at programmed time intervals.

The effluent flowing through one of these ports, an inert gas flow sweeps the others, preventing polymer oxidation.

In the original refractometric detector from Waters, the photocells are placed in the thermostated enclosure which results in a fairly important background noise and a short lifetime at a high temperature. We built a differential refractometer in which only the flow-through cell is located in the heated enclosure.

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TABLE I
Characteristics of Spherosil Silica Beads

Type	Pore diameter, Å
A	<100
B	100–200
C	200–400
D	400–800
E	800–1500
F	~3500
G	~6000

We used, according to the fractionations, 60- or 100-mm-i.d. stainless steel columns. The packing was Spherosil silica gel from Rhône-Progil. The characteristics of the Spherosil gels are reported on Table I.

The dry filling was carried out by applying axial vibrations to the columns. The number of theoretical plates measured using toluene at room temperature was the same whatever the column diameter used: about 3000 per 1.2-m-long column.

EXPERIMENTAL

All this work was done on a high-density polyethylene sample prepared by the Philips procedure. Its characteristics are given in Table III.

We used 1,2,4-trichlorobenzene (TCB) as solvent at 150°C. The flow rate was so adjusted that the linear velocity of the solvent was the same as the one usually used under analytical conditions (i.e., 50 ml/min for 60-mm-i.d. columns).

First, we tried to fractionate this polymer using a column set with a good resolving power in the whole range of molecular weights. This procedure did not give us satisfactory results: the fractions were not narrow enough and those corresponding to the distribution extremities presented a skewed chromatogram in analytical GPC. So, we choose a two-step procedure as shown in Table II. In the first operation, a 3% (weight/volume) polymer solution was separated into three fractions of approximately the same weight using three columns (gels C.D.D.). The characteristics of these 3 primary fractions (F_I, F_{II}, and F_{III}) are reported in Table III.

In the second operation, we fractionated a 1% solution of the F_I fraction using a gel combination of E.E.F.G. We so obtained a 16-fraction series. The
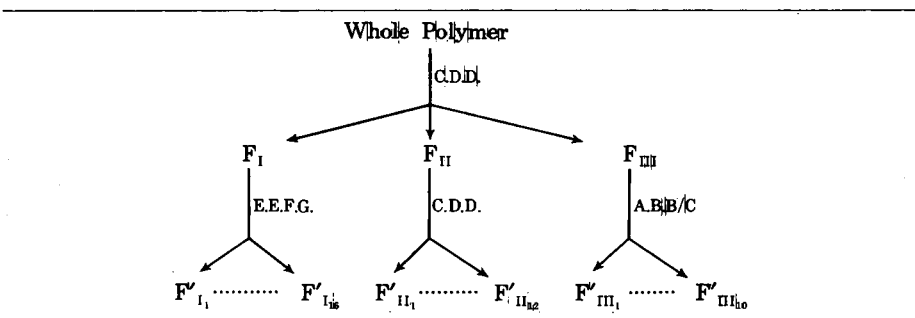
TABLE II
Scheme of Fractionation

Whole Polymer

C.D.D.

F_I F_{II} F_{III}

E.E.F.G.   C.D.D.   A.B.B/C

F'_{I_1} .... $F'_{I_{16}}$ F'_{II_1} .... $F'_{II_{12}}$ F''_{III_1} .... $F''_{III_{10}}$

TABLE III
Characteristics of Primary Fractions

Sample	$\bar{M}_w$	$\bar{M}_n$	P
Whole polymer	98,000	10,000	9.8
F_I	220,000	73,000	3
F_{II}	50,000	25,000	2
F_{III}	12,000	4,000	3

same procedure was carried out on fractions II and III using column combinations C.D.D. and A.B.B./C., respectively.

The characteristics of the 38 fractions so obtained, which are reported in Table IV, were established by analytical GPC measurements, according to the following method.

CHARACTERIZATION OF FRACTIONS

In theory, a complete fraction characterization would entail knowing their molecular weight distribution. In view of the appearance of their chromatograms, which are always shown in the form of narrow gaussian peaks, we will suppose that their distribution follows the Wesslau equation, namely,

$$W(M) = \frac{1}{\sigma(2\pi)^{1/2}} \frac{1}{M} \exp -\frac{1}{2}\left(\frac{\log M/M_0}{\sigma}\right)^2 \tag{1}$$

where σ = standard deviation and M_0 = molecular weight at the apex of the peak.

Thus, the fraction characterization is reduced to the study of the two M_0 and σ parameters which are related to $\bar{M}_w$ (weight-average molecular weight), $\bar{M}_n$ (number-average molecular weight), and $P = \bar{M}_w/\bar{M}_n$ (polydispersity) by the following relations:

$$\bar{M}_w = M_0 \exp \frac{\sigma^2}{2} \tag{2}$$

$$\bar{M}_n = M_0 \exp \frac{-\sigma^2}{2} \tag{3}$$

$$P = \exp \sigma^2. \tag{4}$$

At present, the easiest method for determining these quantities is the analytical GPC. However, it can only give quantitative results if, on one hand, we know the relation between the elution volume and the molecular weight and, on the other hand, the axial dispersion, namely, the shape of the chromatogram corresponding to a perfectly monodisperse polymer.

We will characterize this axial dispersion, supposing it is gaussian, i.e., it obeys the relation

$$y = y_0 \exp \left[-\frac{(V_0 - V)^2}{2\sigma_D{}^2}\right].$$

This evaluation of σ_D was carried out according to the methods of Tung[2] and Hamielec.[3]

TABLE IV
Fractionation Results

Fraction		Weight, g	$M_0 \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	P
F'_I					
	1	0.70	837	909	1.18
	2	0.95	710	768	1.17
	3	1.22	607	656	1.17
	4	1.60	456	491	1.16
	5	2.05	395	423	1.15
	6	2.65	334	357	1.14
	7	3.24	294	314	1.14
	8	3.92	244	260	1.13
	9	4.70	219	234	1.13
	10	5.40	173	184	1.13
	11	6.00	155	165	1.13
	12	6.10	139	148	1.13
	13	5.80	119	127	1.13
	14	4.80	107	114	1.13
	15	3.80	89	95	1.13
	16	2.79	73	78	1.13
F'_{II}					
	1	1.36	186	196	1.11
	2	2.16	162	169	1.10
	3	3.44	118	124	1.10
	4	4.25	93	97	1.10
	5	5.54	74	77	1.09
	6	8.46	59	62	1.09
	7	9.76	49	51	1.09
	8	10.77	36.6	38.4	1.10
	9	11.09	30.0	31.3	1.09
	10	8.78	22.3	23.4	1.10
	11	4.49	14.9	15.7	1.10
	12	2.35	9.9	10.5	1.11
F'_{III}					
	1	15.07	20.0	20.8	1.10
	2	16.38	12.8	13.3	1.10
	3	19.32	8.0	8.3	1.10
	4	14.00	6.5	6.8	1.08
	5	9.48	5.6	5.8	1.08
	6	8.29	4.4	4.6	1.07
	7	5.45	3.9	4.1	1.06
	8	4.62	2.9	3.1	1.06
	9	3.24	2.4	2.6	1.05
	10	3.00	1.7	1.8	1.07

The determination of the molecular weight–elution volume relationship entails knowing the absolute value of the samples molecular weights. For the high molecular weights, the only available method is light scattering, while for the lower molecular weights, we carried out osmotic measurements.

Absolute Measurements

Two research groups, Pétroles d'Aquitaine at Lacq and Centre de Recherches sur les Macromolécules at Strasbourg, carried out measurements on nine of our fractions, covering a broad molecular weight range.
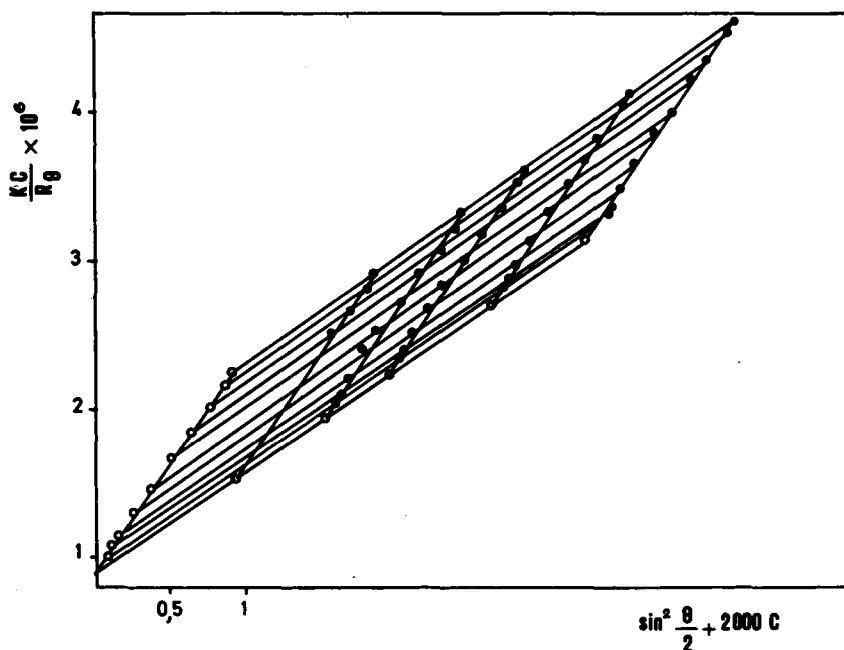
Fig. 1. Zimm plot of reference fraction II.

The light-scattering measurements were carried out using α-chloronaphthalene as solvent between 130 and 145°C. The dn/dc measured values were -0.193 at 135°C and -0.196 at 145°C, which fits in with previous results.[4,5] The solutions were filtered on Millipore HA membranes or porous glass filter G5 Iena type, and decaline or toluene was used as secondary light-scattering standards.[5]

Figure 1 shows the Zimm plot corresponding to the F_{II} fraction. The results are reported in Table V. In this table, we have also reported the limiting viscosity numbers $\{\eta\}$ measured at 135°C in 1,2,4-TCB and the number-average molecular weights $\bar{M}_n$ measured by osmotic pressure using a Mechrolab 502 osmometer. For the latter measurements, we used trichlorobenzene as solvent at 135°C or α-chloronaphthalene at 125°C and Allerfeinst membranes from the Membrangesellschaft (Göttingen).

Finally, the lowest number-average molecular weights were determined by vapor pressure osmometry using a Mechrolab 302 instrument at 130°C and o-dichlorobenzene as solvent.

The agreement between the two series of values obtained for $\bar{M}_w$ is fairly noteworthy, the difficulties of these measurements being well known. Moreover, although the precision in the polydispersity P is low, these measurements confirm the quality of the fractions, i.e., their narrow distribution.

Viscosity–Molecular Weight Relationship

With the viscosities and molecular weights values set, we plotted the curve log $[\eta] = f$ (log M_0) reported on Figure 2. The linear regression according to the least-mean-squares method leads to the values

$$K = 5.26 \times 10^{-4} \quad \alpha = 0.70.$$

TABLE V
Absolute Measurements on Standard Reference Fractions

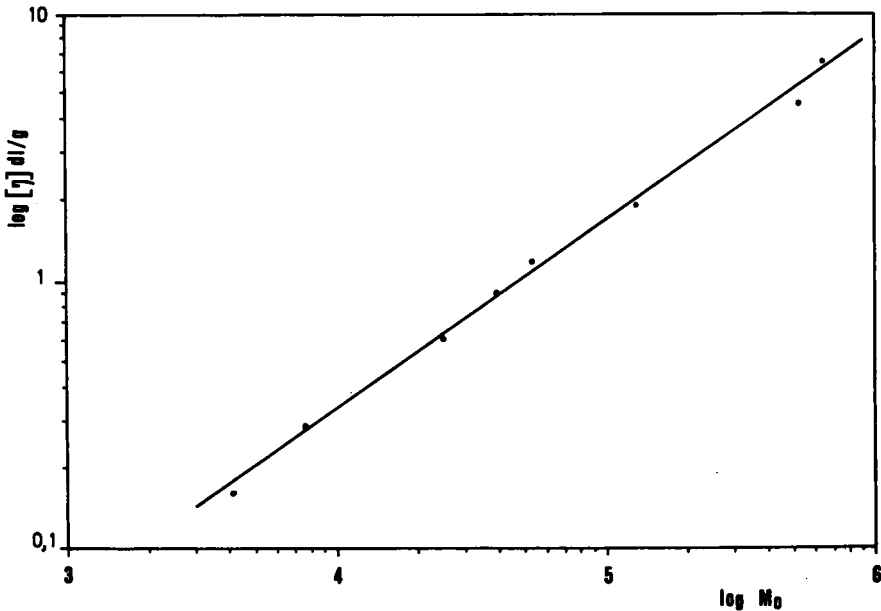| Fraction	$\bar{M}_w$ (LS)			$\bar{M}_n$ (OSM or VPO)	$\bar{M}_w/\bar{M}_n$		$M_0 \times 10^{-3}$	$[\eta]_{TCB}^{135°}$, dl/g
	CRM	SNPA	Average		LS/OSM	GPC		
I	700,000	{693,000 636,000}	676,300	—	—	1.18	623	6.3
II	{570,000 566,000}	520,000	552,000	—	—	1.15	515	4.42
III	—	{135,600 132,900}	134,200	102,000	1.31	1.12	127	1.86
IV	56,500	{54,000 54,200}	54,900	43000	1.27	1.10	52.3	1.15
V	43,600	{39,400 40,100}	41,000	35,500	1.15	1.08	39.5	0.888
VI	32,150	{19,700 25,800}	25,900	22,400	1.15	1.10	24.7	0.604
VII	—	—	—	7420	—	1.10	7.8	0.28
VIII	—	—	—	3920	—	1.06	4.04	0.16
IX	—	—	—	1,870	—	1.07	1.93	—

Fig. 2. Mark-Houwink relationship for fractions of high-density polyethylene.

In a recent paper, Cervenka[6] collected the K and α values obtained by different authors for the same polymer-solvent-temperature system. Our results coincide now with those of Crouzet[7] and are very close to those of Cervenka.[8] So, it seems that after 10 years work, a sure relationship between $[\eta]$ and M has been obtained for linear polyethylene.

Calibration Curve in GPC

A correct calibration curve is obtained plotting $\log M_0$ versus elution volume. The evaluation of M_0 from $\bar{M}_w$ or $\bar{M}_n$ requires the knowledge of the parameter σ, the use of eqs. (2) and (3), and of the well-known relationship

$$\frac{\sigma^2}{a^2} = \sigma_T^2 - \sigma_D^2$$

where σ_T^2 is the total variance calculated from the chromatogram, a is the slope of the calibration curve $\log M_0 = aVe + b$; and σ_D^2 is the variance due to axial dispersion.

In fact, the experiments show that the slope varies little when we replace M_0 by $\bar{M}_w$ for our fraction set. We took for a the value obtained using the latter quantity. The P values so calculated are given in the last column of Table IV.

In our opinion, the agreement between these values and those obtained by direct measurements is satisfactory, considering the possible experimental errors. However, to be even more sure of these values, we refractionated by preparative GPC a fraction of a molecular weight $M_0 = 118,000$ and of a polydispersity $P = 1.1$. We measured the intrinsic viscosity and the weight of each of the four fractions so obtained. This allowed us to calculate, with the aid of the viscosity-molecular weight relationship previously established, the $\bar{M}_w$ and $\bar{M}_n$ values of the original fraction. We so found a polydispersity $P = 1.05$.
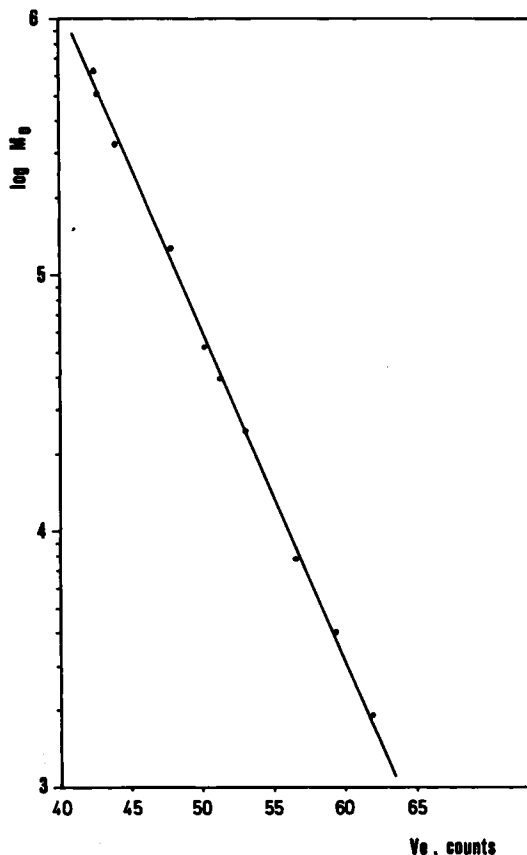
Fig. 3. Calibration curve.

All these results agree very satisfactorily and confirm the indicated poly-dispersity values.

We can now plot the calibration curve as shown in Figure 3. It corresponds to a Spherosil columns set working at 145°C, with a flow rate of 1.5 ml/min and an injection volume of 2 ml of a 0.25% solution (w/v).

Verification of the Calibration Curve

It has been shown that, with all these results, it is possible with only one GPC run to give the precise values of the molecular parameters of every unknown fraction. Dr. Scholte, from D.S.M. Central Laboratorium (The Netherlands), in the program of the working party of the IUPAC Molecular Characterization Committee, measured independently $\bar{M}_w$ by light scattering and $\bar{M}_n$ by osmometry on our fractions. His results are collected in Table VI and compared with the results from our analysis by GPC. The agreement is exceptionally good, justifying "a posteriori" our calibration method.

CONCLUSIONS

In this study, we have described a new preparative liquid chromatography apparatus for the preparation of linear polyethylene fractions. By a two-step

TABLE VI
Verification of the Calibration Curve

Fraction		GPC[a]	Absolute methods[b]
	$\bar{M}_w$	91,000	84,000
A	$\bar{M}_n$	82,800	76,000
	P	1.10	1.1
	$\bar{M}_w$	352,000	358,000
B	$\bar{M}_n$	298,000	285,000
	P	1.18	. 1.25

[a] Our results.

[b] DSM results by osmometry and light scattering; accuracy: $\pm 5\%$ for both $\bar{M}_w$ and $\bar{M}_n$.

procedure, from a polydisperse sample ($\bar{M}_w/\bar{M}_n \sim 10$), narrow fractions can be obtained with molecular weights ranging from 1,500 to 800,000.

These fractions were characterized by viscosity, light scattering, osmometry, as well as analytical GPC measurements. Their polydispersity varies between 1.08 and 1.18 according to their molecular weight.

These fractions, which are now available commercially (Société Nationale des Pétroles d'Aquitaine, 92080, Courbevoie, France) allow precise calibration of any analytical GPC apparatus, giving both the calibration curve log $(M) = f (V_e)$ and the axial dispersion of the system.

References

1. A. Peyrouset and R. Panaris, *J. Appl. Polym. Sci.*, **16**, 315 (1972).
2. L. H. Tung and J. R. Runyon, *J. Appl. Polym. Sci.*, **13**, 2397 (1969).
3. A. E. Hamielec and W. H. Ray, *J. Appl. Polym. Sci.*, **13**, 1317 (1969).
4. H. L. Wagner and C. A. J. Hoeve, *J. Appl. Polym. Sci. A-2*, **9**, 1963 (1971).
5. J. Ehl, C. Loucheux, C. Reiss, and H. Benoit, *Makromol. Chem.*, **75**, 35 (1964).
6. G. R. Williamson and A. Cervenka, *Eur. Polym. J.*, **8**, 1009 (1972).
7. P. Crouzet, A. Martens, and P. Mangin, 7th International GPC Seminar, Monte Carlo, 1969.
8. A. Cervenka, *Makromol. Chem.*, **170**, 239 (1973).