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SECOND REPORT OF THE IUPAC WORKING PARTY ON THE MOLECULAR CHARACTERIZATION OF COMMERCIAL POLYMERS

MOLECULAR CHARACTERIZATION OF POLYETHYLENE

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MOLECULAR CHARACTERIZATION OF POLYETHYLENE
Second Report of the IUPAC Working Party on the Molecular Characterization
of Commercial Polymers

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1. INTRODUCTION

With an aim to integrate the molecular characterization methods used for polymers in
solution in different laboratories, and to get an impression of the absolute accuracy of
the data so obtained, various investigations (1,2) have been made in the last few
decennia. In 1971 a Working Party was formed under the auspices of the IUPAC to make a more
conscious study of the molecular characterization methods. One of the purposes was to
achieve a higher level of agreement between the results of polyethylene characterization
methods than was obtained in the 1970 investigation (2). The Working Party was concerned
with viscometry, osmometry, light scattering, equilibrium ultracentrifugation, and gel
permeation chromatography on linear and branched polyethylene, and covered both whole
polymers and fractions. Results up to 1974 were reported (3).
Before proceeding to other polyolefines, two commercial low-density polyethylenes were
investigated to get a picture of the state of the art concerning polyethylene. This report
describes the results of that investigation. The samples were characterized by the same
methods but with different instruments, different calibration methods and in different
laboratories (Note a). All results were compared in order to establish the range in which
different institutes can be expected to achieve the same results. The investigation
included work on molecular weight parameters and the detection of branching.

2. PRODUCT DESCRIPTION

The samples investigated were two commercial branched low-density polyethylenes, provided
by DSM and checked to be sufficiently homogeneous. They will be designated here as sample α
and sample β. Melt indices and densities are given in Table 1.

TABLE 1. Melt indices and densities of the two samples

	Melt index (g/10')	Density (g/cm^3)
Sample α	1.7	0.9202
Sample β	2.2	0.9236

Figure 1 shows the GP chromatograms of both products, obtained with a Waters 200 GPC
apparatus in 1,2,4 -trichlorobenzene (TCB) at 135 $^\circ$C over five columns filled with styragel.
Figure 2 shows the Zimm plots for light scattering in α-chloronaphthalene (αCN) at 145 $^\circ$C
after dissolution for three hours at 145 $^\circ$C under mild stirring; measurement was made with
a Sofica 42000 M light scattering photometer.

Note a. Participants in this investigation were:

BASF, Ludwigshafen (Dr. Ball)
CdF Chimie, Mazingarbe (Dr. Constantin)
CRM, Strasbourg (Professor Benoit, Dr. Strazielle)
Chalmers TH, Göteborg (Dr. Holström)
DSM, Geleen (Dr. Scholte)
CW Hüls, Marl (Dr. Meyer)
Pekema OY, Kulloo (Dr. Starck)
Saga Petrochemicals, Oslo (Dr. Grande)
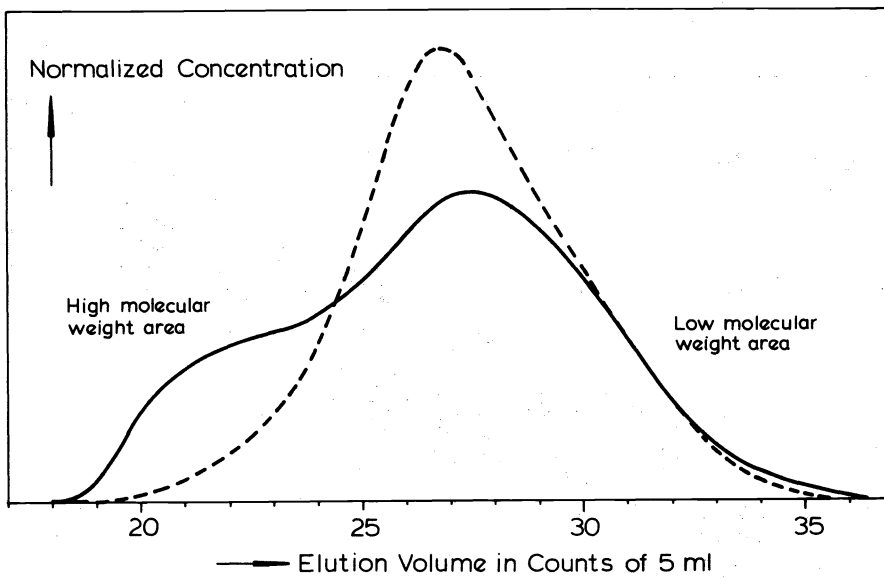SNPA, Lacq (Dr. Prechner)

Normalized Concentration

High molecular
weight area

Low molecular
weight area

20   25   30   35

Elution Volume in Counts of 5 ml

Fig. 1. Gel Permeation Chromatograms of the two samples.
———— sample α
– – – – sample β

$\frac{Kc}{R_\theta} \times 10^6$ (mole g^{-1})

5 –

4 –

3 –

2 –

1 –

0 –

$\sin^2 \frac{\theta}{2} + 10^3 C$

0   1   2   3   4   5   6   7
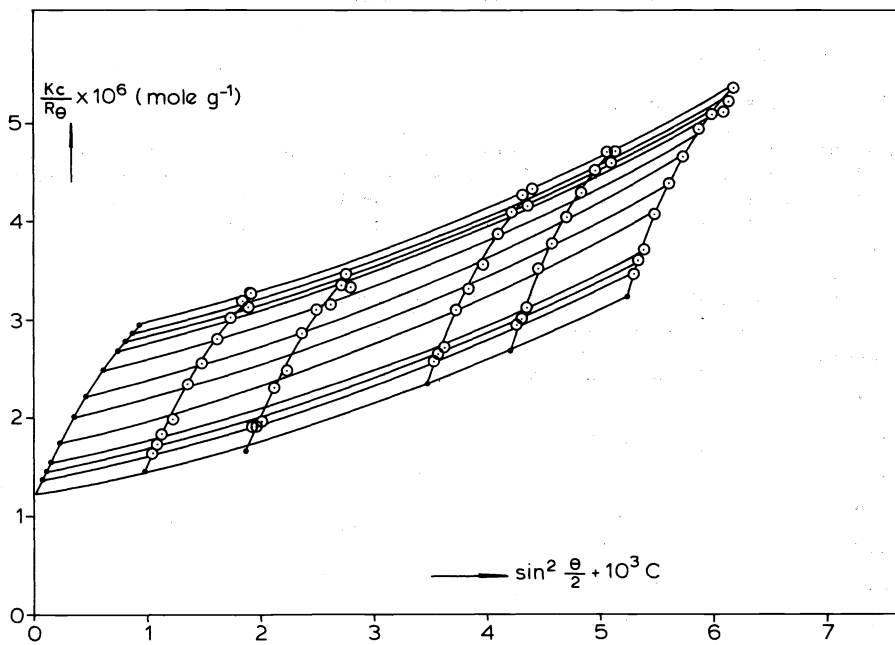
Fig. 2a. Light scattering Zimm plot of sample α.
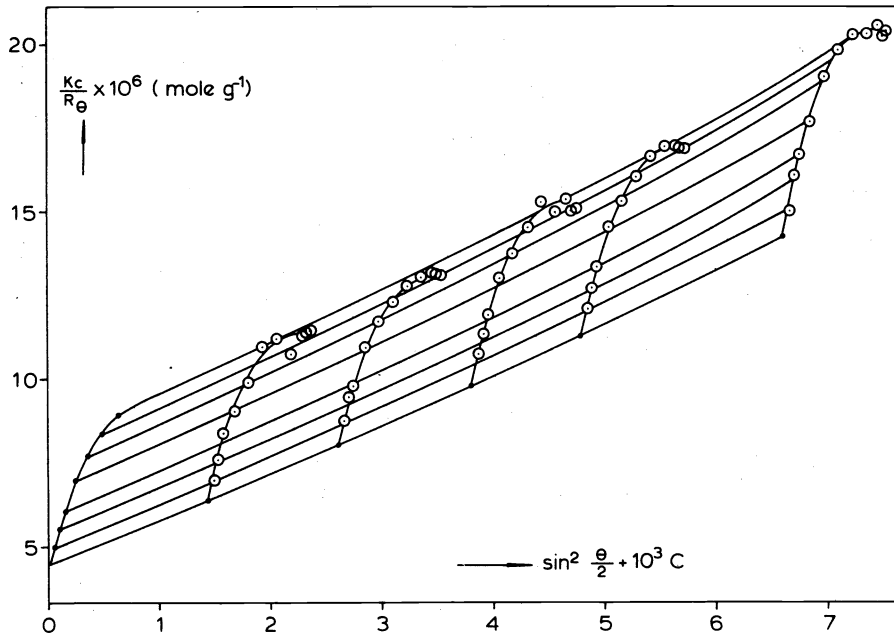
Fig. 2b. Light scattering Zimm plot of sample β.

3. CHARACTERIZATION

3.1. Intrinsic Viscosity

All participants used capillary viscometers of the Ubbelohde type. In a number of cases the automatic viscometer Fica 52 was used. Measurements were carried out using solutions of different concentrations in TCB at 135 $^{\circ}$C. The extrapolation to concentration zero, necessary to obtain the intrinsic viscosity $[\eta]$, was done by each investigator in his own way. The results are listed in Table 2.

TABLE 2. Intrinsic viscosities of the two samples in TCB at 135 $^{\circ}$C (dl/g)

Sample α	Sample β
1.12	0.91
1.08	0.94
1.12	0.92
1.05	0.88
1.07	0.91
1.14	0.92
1.05	0.88
1.07	0.92

They can be summarized as follows:

Sample α: $[\eta]_{TCB}^{135^{\circ}} = 1.09_{-0.04}^{+0.05}$ (Note a)   Deviation from average value < 5 %

Sample β: $[\eta]_{TCB}^{135^{\circ}} = 0.91_{-0.03}^{+0.03}$ Deviation from average value < 4 %

Note a. Here supercript and subscript mean maximum deviation to the higher and to the lower side, respectively.

Deviations from the mean value do not exceed 5 %, a significant improvement over former investigations (2,3).

3.2. Number Average Molecular Weight

The number average molecular weight of the samples was measured by membrane osmometry. Only three participating laboratories performed these measurements. Different types of osmometers were used; the membranes employed were "Ultracella allerfeinst" or "Schleicher Schuell 08". It is very well possible that some of the M_n values came out too high because to diffusion of the smallest molecules through the membrane.

TABLE 3. Number average molecular weights by membrane osmometry

Experimental conditions	Sample α	Sample β
TCB, 115 $^{\circ}$C	31×10^3	26×10^3
αCN, 125 $^{\circ}$C	20.5×10^3	26.8×10^3
Tetraline, 120 $^{\circ}$C	30×10^3	23.5×10^3

Table 3 shows the results which can be summarized as follows:

Sample α: $10^{-3} x M_n = 27.2^{+3.8}_{-6.7}$ Deviation from average value < 25 %

Sample β: $10^{-3} x M_n = 25.4^{+1.4}_{-1.9}$ Deviation from average value < 8 %

3.3. Weight Average Molecular Weight

Although light scattering was the method used at all laboratories, different apparatus, different solvents, different temperatures and different methods for calibrating the instruments were employed.

TABLE 4. Weight average molecular weight by light scattering

Experimental conditions	Sample α $10^{-3} x M_w$	Sample β $10^{-3} x M_w$
αCN, 140 $^{\circ}$C	830	220
TCB, 135 $^{\circ}$C	950	248
αCN, 140 $^{\circ}$C	805	165
αCN, 140 $^{\circ}$C	640	160
	640	143
αCN, 145 $^{\circ}$C	785	204
αCN, 145 $^{\circ}$C	770	200

The measuring conditions and the results are listed in Table 4. They can be summarized as follows:

Sample α: $10^{-3} x M_w = 774^{+176}_{-134}$ Deviation from average value < 23 %

Sample β: $10^{-3} x M_w = 191^{+57}_{-48}$ Deviation from average value < 30 %

3.4. Structure Parameters

The numbers of methyl, vinyl and vinylidene groups per 1000 carbon atoms as determined by infrared analysis in four laboratories are listed in Table 5.

TABLE 5. Structure parameters by infrared analysis

Sample α			Sample β		
CH_3/1000 C	Vinyl Groups/ 1000 C	Vinylidene groups/1000 C	CH_3/1000 C	Vinyl Groups/ 1000 C	Vinylidene groups/1000 C
26	0.1	0.4	24	0.11	0.4
25.2	< 0.1	≤ 0.3	23.1	< 0.1	≤ 0.3
23.9			22.1		
20	0.2	≤ 0.3	21	0.2	

The instruments, the methods of calibration and the calibration standards were freely chosen.
Only the CH_3 contents permit a quantitative comparison. The results can be summarized as follows:

Sample α: CH_3/1000 C = 24^{+2}_{-4} Deviation from the average value < 16 %

Sample β: CH_3/1000 C = 23^{+1}_{-2} Deviation from the average value < 10 %

3.5. Gel Permeation Chromatography

All participants used the Waters GPC apparatus (model 200) at 135-150 $^{\circ}$C. The solvent was 1,2,4-trichlorobenzene or o-dichlorobenzene with concentrations ranging from 1.10^{-3} to 4.10^{-3} g/ml. Column packings and numbers of columns were different; both styragel and porous glass fillings were used.
The methods of calibration were different. Some participants calibrated their instruments with a series of narrow polystyrene samples and used the universal calibration principle (4) to convert this calibration to that of linear polyethylene. Other participants calibrated with a series of narrow linear polyethylene fractions of known molecular weight or with a few broad polyethylene samples of which both M_n and M_w were known. In some cases both methods were used together. One investigator calibrated his apparatus with samples of branched polyethylene of a given density and assumed that the deviation of the GPC calibration curve from that of linear polyethylene was mainly dependent on density.

3.5.1. Determination of Apparent Number and Weight Average Molecular Weights (M_n^* and M_w^*)

At first the apparent values M_n^* and M_w^* of the number average and the weight average molecular weights determined by GP chromatography calibrated for linear polyethylene were compared. No correction for axial dispersion was made.

TABLE 6. Apparent molecular weights by GPC

Sample α		Sample β	
$10^{-3}\times M_n^*$	$10^{-3}\times M_w^*$	$10^{-3}\times M_n^*$	$10^{-3}\times M_w^*$
14	228	15	86
22.4	203	23.9	97.6
19.2	228	19.4	91.7
23	239	22	100
24	200	24	96
31	220	28	99
21	250	21.5	108

Table 6 lists the results which can be summarized as follows:

Sample α: $10^{-3} \times M_n^* = 22^{+9}_{-8}$ Deviation from average value < 40 %

Sample β: $10^{-3} \times M_n^* = 22^{+6}_{-7}$ Deviation from average value < 32 %

Sample α: $10^{-3} \times M_w^* = 224^{+26}_{-24}$ Deviation from average value < 12 %

Sample β: $10^{-3} \times M_w^* = 97^{+11}_{-11}$ Deviation from average value < 12 %

The relative deviations of M_n^* are much greater than those of M_w^*. One of the reasons is that the procedure for subtraction of the base line from the chromatogram is much more sensitive at the edges than in the middle part of the chromatogram. Another reason is that the determination of M_w^* mainly uses parts of the linear middle section of the calibration curve. Determination of M_n^*, on the other hand, also uses a curved part of the calibration curve, which is not nearly as accurately fixed as the straight part.

3.5.2. Determination of Absolute Number and Weight Average Molecular Weights (M_n and M_w)

The apparent molecular weight averages were corrected to give the absolute values M_n and M_w. Most participants employed the Drott-Mendelson iteration method to determine the branching density λ that equalized the calculated intrinsic viscosity of the whole polymer and the measured value. They used different values for the Mark-Houwink equation constants K and a and different values for the exponent b in the relation $g' = g^b$.

TABLE 7. Absolute molecular weights bij GPC

Correction Method	Sample α		Sample β	
	$10^{-3} \times M_n$	$10^{-3} \times M_w$	$10^{-3} \times M_n$	$10^{-3} \times M_w$
Drott-Mendelson, b = 0.8	26	950		
Drott-Mendelson, b = 0.5	26.3	657	20.3	194
Drott-Mendelson, b = 0.5	21.2	723	21.2	170
Drott-Mendelson, b = 0.5	30	980	26	241
Correction for each count	26.6	1050	25.9	234
Calibration with branched samples	26.6	1160	20.2	226

The results of this correction method are listed in Table 7. One of the participants measured the intrinsic viscosity of each fraction and corrected M^* of that fraction for branching, starting from the matching $[\eta]$ value. Another participant calibrated his GP chromatograph with branched PE fractions and used the calibration curve for the LDPE samples. The results can be summarized as follows:

Sample α: $10^{-3} \times M_n = 26^{+4}_{-4.8}$ Deviation from average value < 20 %

Sample β: $10^{-3} \times M_n = 23^{+3}_{-2.8}$ Deviation from average value < 13 %

Sample α: $10^{-3} \times M_w = 920^{+240}_{-263}$ Deviation from average value < 28 %

Sample β: $10^{-3} \times M_w = 213^{+28}_{-43}$ Deviation from average value < 20 %

A comparison of the average values M_n and M_w from GPC with those from the absolute methods of osmometry and light scattering is made in Table 8. The difference between the mean values is 5-10 % for M_n and 10-17 % for M_w. The institutes with the highest M_w values from light scattering also have the highest M_w values from GPC, and vice versa, as is to be expected from the GPC calibration (Table 9).

TABLE 8. Mean values of M_n and M_w by absolute methods and by GPC

	Sample α	Sample β
$M_n^{\mathbf{x}}$ by GPC	22×10^3	22×10^3
M_n by GPC	26×10^3	23×10^3
M_n by osmometry	27.2×10^3	25.4×10^3
$M_w^{\mathbf{x}}$ by GPC	224×10^3	97×10^3
M_w by GPC	920×10^3	213×10^3
M_w by light scattering	774×10^3	191×10^3

TABLE 9. Comparison of M_w values as determined by light scattering and by GPC

	Sample α		Sample β	
	LS	GPC	LS	GPC
Laboratory 1	950×10^3	1160×10^3	248×10^3	226×10^3
Laboratory 2	830×10^3	950×10^3	-	-
Laboratory 3	805×10^3	723×10^3	165×10^3	170×10^3

4. DISCUSSION AND CONCLUSIONS

Comparison of the values reported by the participating laboratories for intrinsic viscosity, absolute molecular weights and short chain branching of low-density polyethylene reveals closer agreement than was found in earlier investigations (1,2). This result was achieved in spite of the fact that the participants used different types of equipment and methods as well as different ways of calibration and data treatment. It indicates the improvements achieved in this field over the last few years as a consequence of, for example, the high technical standard of equipment, better sample preparation and sample treatment, and availability of well-identified standard samples (3).
Comparison of the absolute molecular weights determined by GPC, light scattering and osmometry shows that the M_w values from light scattering are lower than those from GPC, while the differences between the number average molecular weights determined by GPC and osmometry are within the experimental error. Differences between weight average molecular weights are lower at lower molecular weights, which points to a low accuracy of the (generally extrapolated) high-molecular weight part of the calibration curves of the participants.
The agreement between the absolute molecular weights of "commercial low-density polyethylene" is sufficient, though not quite satisfactory. However, differences between the measured data can be expected to decrease when all participants use the same type of equipment under the same conditions as well as identical methods of calibration and data treatment.

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