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**MOLECULAR
CHARACTERIZATION
OF POLYETHYLENE**

*A Report of the IUPAC Working Party on the Molecular
Characterization of Commercial Polymers*

Prepared for publication by

CLAUDE STRAZIELLE

CNRS, Strasbourg, France

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MOLECULAR CHARACTERIZATION OF COMMERCIAL POLYMERS

CLAUDE STRAZIELLE

*Centre de Recherches sur les Macromolécules, CNRS,
6 rue Boussingault, 67083 Strasbourg CEDEX, France*

This report of the IUPAC Working Party on the Molecular Characterization of Commercial Polymers describes the results of an international collaborative study carried out by eleven laboratories. It was presented at the IUPAC Symposium on Macromolecules at Madrid in September 1974 by the author.

In the framework of the first Working Party on the 'Molecular Characterization of Commercial Polymers', five polymers were investigated by means of classical techniques for solutions (osmometry, viscosity, light scattering and gel permeation chromatography). These polymers were: one sample of polystyrene (PS), one sample of polyvinyl chloride (PVC), one sample of polyvinylacetate (PVA_c) and some samples of high density polyethylene (HDPE) and low density polyethylene (LDPE).

The results of this first Working Party were reported during the IUPAC Symposium at Leiden (1970)¹. The viscosity values for all the samples were in good agreement, but some discrepancies in the determination of the weight average molecular weight (by light scattering and GPC) were observed. The variations in the M_w values were considerable in some cases as shown in *Table 1*. This table gives M_w values from light scattering and GPC for LDPE sample A, B and C. (About fifteen laboratories investigated these samples.)

Table 1. Weight average molecular weight values for LDPE, samples A, B and C

$M_w(\text{LS})$			$M_w(\text{GPC})$		
A	B	C	A	B	C
1.24×10^6	580000	750000			
			177000	254000	136000
			54000	39000	23900
3×10^6	606000	1.02×10^6			
795000	425000	425000			
			415000	492000	449000
$\left\{ \begin{array}{l} 2.3 \times 10^6 \\ 2.3 \times 10^6 \\ 6 \times 10^6 \\ 1.06 \times 10^6 \end{array} \right.$	$\left\{ \begin{array}{l} 600000 \\ 560000 \\ 730000 \\ 570000 \end{array} \right.$	$\left\{ \begin{array}{l} 1.4 \times 10^6 \\ 1.25 \times 10^6 \\ 1.6 \times 10^6 \end{array} \right.$			
2.3×10^6	600000	810000			
1.4×10^6					
			248000	530000	282000
			247000	233000	233000
			244000	313000	259000

These results indicated that our knowledge of the molecular characterization of LDPE was still unsatisfactory and reflected the general situation in the field of branched polymers. It was interesting to continue this Working Party by considering the problem of the 'Characterization of Polyethylenes'.

The new programme was set up in order, first, to obtain more accurate and more consistent measurements by means of dilute solution techniques; secondly, to have a more accurate method for the correction of long chain branching by GPC; and, thirdly, to determine, if possible, the index of branching for LDPE.

This report summarizes the results obtained from eleven laboratories which have participated in this Working Party*. The samples are two unfractionated polyethylenes of broad molecular weight distribution: the first is one HDPE sample (Eltex 6009 from Solvay) and the second is one LDPE sample from BASF, the same LDPE B that was studied in the first Working Party. Both unfractionated samples were homogenized. We have also characterized some fractions of an LDPE B sample obtained by preparative GPC.

The techniques used were: viscosity, osmometry and light scattering, but it is essentially the problem of the characterization by GPC which has been examined here.

In order to compare all the results easily, the following experimental conditions were chosen: the viscosity and GPC measurements were made under the same conditions: in trichlorobenzene (TCB) at 135°C. The determination of M_n by osmometry was made in TCB or α -chloronaphthalene at 130°C, and the weight average molecular weight M_w by means of light scattering was determined at 125° in α -chloronaphthalene with 0.1 per cent ionol as antioxidant (the refractive index increment dn/dc is $-0.196 \text{ cm}^3/\text{g}$ for $\lambda = 546 \text{ nm}$).

(A) STUDY OF HIGH DENSITY POLYETHYLENE

For the characterization of polydisperse linear and branched polyethylene by means of GPC, some well defined fractions of linear PE are needed in order to establish the calibration curves of $\log M$ and $\log (\eta M)$ as functions of the elution volume v_e , and to determine accurate values for k and a parameter of the viscosity/molecular weight relationship $[\eta] = kM^a$.

* The participants in this IUPAC programme were:

- (1) BASF, Ludwigshafen (Dr Ball)
- (2) Compagnie Française de Raffinage, Harfleur (Dr Verschave)
- (3) Chalmers Teknika Högskola, Göteborg (Dr Holmström)
- (4) Dutch State Mines, Geleen (Dr Scholte)
- (5) Ethylène-Plastique, Mazingarbe (Dr Assioma)
- (6) Chemische Werke Hüls, Recklinghausen (Dr Glenz)
- (7) Montecatini Edison, Milan (Dr Mula)
- (8) Naphtachimie, Lavera (Dr Crouzet)
- (9) Société Nationale des Pétroles d'Aquitaine, Lacq (Dr Panaris)
- (10) Solvay, Bruxelles (Dr Servotte)
- (11) Centre de Recherches sur les Macromolécules, Strasbourg (Professor Benoît).

(a) Fractionation of polyethylenes by preparative GPC

The fractionation of (high density and low density) polyethylene was achieved by using the preparative GPC technique. The experiments were carried out by Dr Panaris and Dr Peyrouset from the Société Nationale des Pétroles d'Aquitaine with an apparatus which allows the fractionation of about 20 g of polymer per day. This preparative GPC built in the research centre of SNPA can be divided into five components exactly as for the analytical GPC apparatus: pumping system, sample injector, columns, detector and fraction collector. Details of this apparatus were published recently². However, it is interesting to cite some experimental conditions.

The sample injector allows introduction of 100 ml of solution each time. The columns used were a set of six, each containing spherosil type B-B/C-D-E-F and G.

Fractionation is obtained of 50 g of PE dissolved in TCB at one per cent concentration (+ 1 per cent of antioxidant). For each manipulation 100 ml (or 1 g) is fractionated at 150°C with a flowrate of 50 ml per minute and the volume of each fraction is 250 ml.

All of each fraction is collected, concentrated by evaporation and precipitated.

Fractionation of HDPE was done in two steps. The first gave three fractions (of low, intermediate and high molecular weight); in the second step these fractions were refractionated into several fractions.

Table 2. Characterization of linear PE fractions (obtained by preparative GPC: SNPA)

Fraction	M_n (osm.)	M_w (LS)	$[\eta]$ dl/g
A	22600	32200	$\left\{ \begin{array}{l} 25800 \\ 19700 \end{array} \right.$ 0.604
B	34500	43600	$\left\{ \begin{array}{l} 39400 \\ 40100 \end{array} \right.$ 0.888
C	43500	56500	$\left\{ \begin{array}{l} 54000 \\ 54200 \end{array} \right.$ 1.15
D	102000	107500	$\left\{ \begin{array}{l} 135600 \\ 132900 \end{array} \right.$ 1.86
E	—	$\left\{ \begin{array}{l} 570000 \\ 506000 \end{array} \right.$	520000 4.42
F	—	700000	$\left\{ \begin{array}{l} 690000 \\ 636000 \end{array} \right.$ 6.0

Table 2 shows the molecular parameters of some linear polyethylene fractions obtained in this way. The viscosity values $[\eta]$, the number average molecular weight M_n by osmometry, and the weight average molecular weight determined by means of light scattering from three different measurements all appear in Table 2. The degree of polydispersity or the ratio M_w/M_n of the different fractions determined by analytical GPC is about 1.08.

These fractions obtained from preparative GPC can be used as reference material to establish the calibration curve of analytical GPC.

In addition from these results, one can determine the Mark-Houwink

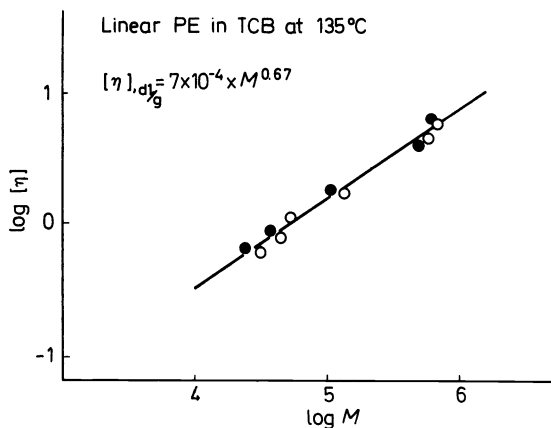


Figure 1

relation for linear PE in TCB at 135°. This relation is shown in the Figure 1 ($k = 7 \times 10^{-4}$ and $a = 0.67$).

(b) Mark-Houwink relation for linear PE

It was noted above that it is very important to have accurate values of k and a in the Mark-Houwink equation if the GPC chromatograms of HDPE or LDPE are interpreted via the 'Universal Calibration Curve', $\log(\eta M)$ as a function of v_e . For instance, in the case of a branched polymer of mass M_b and viscosity $[\eta]_b$, we can write

$$[\eta]_b M_b = [\eta]_L M_L \quad (\text{at constant elution volume})$$

M_L is the molecular weight of the linear polymer which is eluted at the same elution volume as the branched polymer; $[\eta]_L$ is the viscosity of the linear polymer and can be calculated by using the Mark-Houwink relation.

We can find in the literature³ several studies relative to the viscometric behaviour of linear PE in TCB at 135°.

 Table 3. Viscosity: values of k and a for linear PE in TCB at 135°C

Workers	$k \times 10^4$	a	Workers	$k \times 10^4$	a
Crouzet <i>et al.</i>	5.23	0.70	Wild <i>et al.</i>	3.23	0.735
Thiery-Cousin	15.0	0.60	Prechner <i>et al.</i>	12.7	0.61
Drott-Mendelson	4.6	0.725	Williamson-Cervenka	9.54	0.64
Cote-Shida	7.1	0.67	Ball (report WP 71)	8.1	0.64
Otocka <i>et al.</i>	5.1	0.70	Prechner (report WP 72)	7.1	0.67
Miltz-Ram	5.96	0.70	Cervenka (report WP 72)	5.2	0.66

In Table 3 we have collected the different values of k and a . These parameters are not very well defined. The k values vary in the range from 4.6 to 15×10^{-4} and the a values in the range from 0.6 to 0.72. This leads to a discrepancy in the determination of the molecular weight of about 30 per

cent. From these results, it is difficult to choose an accurate pair of k and a values: some experimentors use the values of 7 or 8 for k and 0.67 for a , and others prefer to use 0.70 or 0.72 for a .

It is also noteworthy that the universal calibration curve can be obtained from fractions of polystyrene and polyethylene. In the case of polystyrene in TCB at 135°C, the Mark-Houwink relation given by Williamson and Cervenka⁴ is

$$\eta = 1.72 \times 10^{-4} M^{0.67}$$

The use of linear polystyrene fractions for the determination of the calibration curve in GPC is interesting especially in the range of high molecular weights ($M > 10^6$).

(c) Study of the unfractionated HDPE sample

This section presents the analysis of the results obtained by the different participants on the unfractionated high density polyethylene sample.

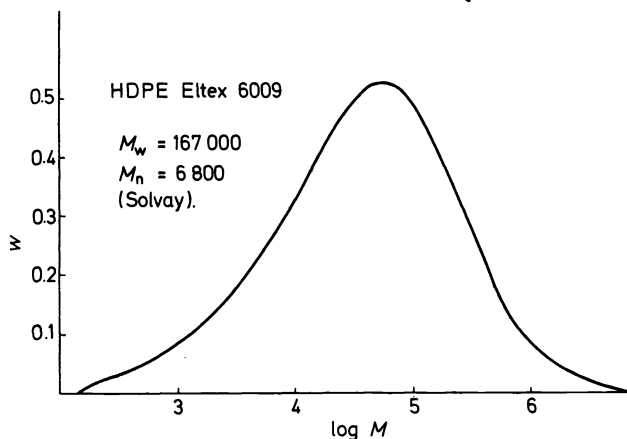


Figure 2

This sample has a very high degree of polydispersity as shown in *Figure 2*. The figure gives the molecular weight distribution obtained from the GPC experiments (from Solvay). The sample contains a non-negligible fraction of low molecular weight below ten thousand. The molecular parameters of this sample determined by eight laboratories are collected in *Table 4*.

In general, the viscosity values and the values of M_n and M_w from GPC are in good agreement except, perhaps, one or two values. The weight average molecular weight M_w from light scattering data (and also ultracentrifugation) is determined with good precision: about ± 8 per cent. On the other hand, the M_w value from GPC is slightly higher than the M_w value from LS but the agreement between the two values is satisfactory: the difference is about seven per cent.

However, we observe some values which seem not to be correct: for instance, the M_n value obtained from osmometry is higher. This fact can be

Table 4. Molecular parameters of unfractionated HDPE (Eltex 6009 sample)

Sample No.	[η]dl/g	M_n		M_w	
		osm.	GPC	LS	GPC
2	1.51		12500		127000
3	1.69		12000		185000
4	1.77	21000	9100	154000 179000 160000(u.c.)	190000
5			9000		208000
7	1.68		10500		130000
8	1.87		11000		210000
9	1.51		10500	165000 179000	201000
10	1.83		6800		164000
Av.	1.69		10100	166000	178000

explained by considering the diffusion of the molecules of low molecular weight through the membrane.

To conclude this study on HDPE, it seems from these results that the characterization of HDPE (whole polymer and *a fortiori* fractions) can be carried out without insuperable difficulties.

(B) STUDY OF LOW DENSITY POLYETHYLENE

The interpretation of GPC measurements on low density polyethylene is much more complicated than was the case with linear HDPE. This is because LDPE is composed of molecules having not only different molecular weights but also various numbers of long-chain branchings which affect the GPC measurements. From one calibration curve of log M established with linear polyethylene fractions, we obtain an apparent value for M_w which is corrected to long-chain branching by using the combination of viscosity and GPC data. In order to examine this point, we have studied to start with, some LDPE fractions. These fractions were obtained by preparative GPC from the LDPE B sample studied by the preceding Working Party. The experimental conditions for this fractionation were identical to the conditions used for the HDPE fractionation; but the fractions were obtained from one step only.

From 50g of the LDPE B sample, about twenty fractions were collected, but only seven intermediate fractions were studied: these fractions are designated $F_6, F_7, F_8, F_{10}, F_{12}, F_{14}, F_{16}$. The chromatograms of the fractions appear in *Figure 3*.

The results of the viscosity and GPC measurements for each fraction are summarized in *Tables 5 and 6*. *Table 5* shows the [η] values in TCB at 135°C obtained by the different laboratories. Also given are the average $\langle [\eta] \rangle$ value for each fraction. As for the HDPE samples, the results are in relatively good agreement (except perhaps one or two series of values which are lower): the viscosity [η] is obtained with a precision of about ten per cent.

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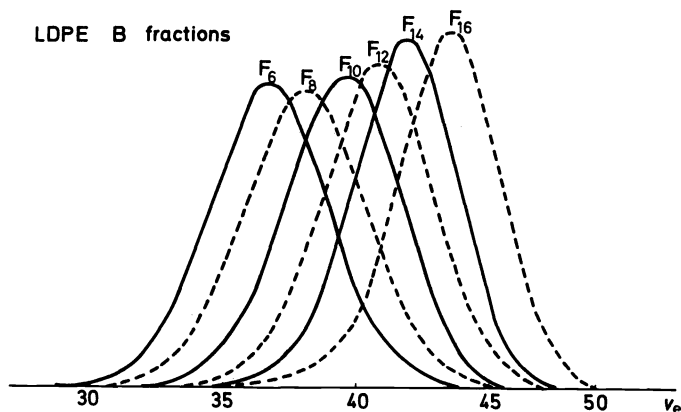


Figure 3

Table 5. Intrinsic viscosity values of LDPE B fractions.

No.	Fr.	6	7	8	10	12	14	16
	1	—	1.62	1.41	1.12	0.85	0.64	0.48
2	1.57	—	1.25	1.08	0.76	0.57	0.48	
3	1.65	—	1.34	1.03	0.82	0.63	0.46	
4	—	1.51	1.39	1.07	0.81	0.65	0.46	
5	1.61	—	1.23	0.92	0.69	0.51	0.38	
6	—	1.70	1.45	1.15	0.90	0.65	0.50	
8	1.71	—	1.38	1.08	0.83	0.63	0.47	
9	1.76	1.45	1.29	1.00	0.77	0.60	0.39	
10	1.74	1.60	1.37	1.11	0.86	0.66	0.49	
Av.		1.67	1.58	1.35	1.06	0.81	0.62	0.46

 Table 6. M_w^{GPC} apparent values of LDPE B fractions

No.	Fr.	6	7	8	10	12	14	16
	2	190		134	89	64	45	32
3	236		141	99	63	39	24	
4		182	143	91	52	33	22.5	
5	254		158	101	64	39	23	
6	188		148	98	64	29	27	
8	291		150	125	78	55	35	
9	248	218	180	118	73	43	21	
10	220	175	138	85	50	34	18	
Av.		232	192	149	100	64	40	25

In *Table 6*, the results for the apparent molecular weight M_w^{app} obtained from GPC are set out. These values were obtained by using the calibration curve $\log M$ as a function of elution volume v_e established with the linear PE.

These apparent M_w values obtained with a precision of about 15 to 20 per cent are consistent if one considers that the set of columns, the packing material (spherosil or styrigel) and the method of establishing the calibration curve are different from one experiment to another.

Now, some people have tried to determine the weight average molecular weight after correction of the long-chain branching effect. This correction has been made by combining the viscometric and GPC data, or, in one case, by using a calibration curve established from branched polyethylene samples.

Table 7. Molecular weights (M_n , M_w) of LDPE B fractions

Fraction No.	$M_n \times 10^{-3}$ osm.	$M_w \times 10^{-3}$ LS-UC	$M_w \times 10^{-3}$ GPC (av.)	$M_w \times 10^{-3}$ GPC (calc.)
6	278	400	440	$\begin{cases} 550 \\ 335 \end{cases}$ 400
7	178	355	—	294
8	160	275	300	$\begin{cases} 378 \\ 230 \end{cases}$ 225
10	85	176	185	$\begin{cases} 243 \\ 127 \end{cases}$ 147
12	47	108	113	$\begin{cases} 97 \\ 140 \end{cases}$ 92
14	29	43	66	$\begin{cases} 56 \\ 80 \end{cases}$ 54
16	17	24	36	$\begin{cases} 25 \\ 41 \end{cases}$ 33

The average value of M_w^{GPC} and the extreme value for each fraction are reported in *Table 7* and compared with some M_w values obtained by light scattering or ultracentrifugation methods. It should be noted here that these M_w values are obtained from three or four different measurements; the agreement between these results is not good especially for two series of values obtained by light scattering (see report November 1973) and it has not yet been possible to explain this discrepancy.

The M_w^{GPC} values given in the last column of *Table 7* were calculated by combining the average values of the viscosity and GPC obtained by all the participants

$$M_{w, \text{calc.}} = \{[\eta]_{\text{L}}^{v_e} / [\eta]_{\text{b, av.}}\} (M_w)_{\text{L, av.}}$$

where $(M_w)_{\text{L}}$ is the molecular weight of the linear PE at the same elution volume v_e . In order to calculate $[\eta]_{\text{L}}^{v_e}$, we used $k = 7 \times 10^{-4}$ and $a = 0.67$ in the Mark-Houwink equation.

The divergence between the values of M_w from GPC and light scattering or ultracentrifugation is not very large.

In *Table 7*, we also give the M_n values. They are an average of two results which are in good agreement (five per cent).

The determination of the branching index g' for each fraction is shown in

Table 8. Evaluation of branching index by GPC and viscosity.

$$g'_n = \frac{[\eta]_b}{[\eta]_l} \text{ at constant molecular mass.}$$

or

$$g'_n = \left(\frac{[\eta]_b}{[\eta]^*} \right)^{1+a} \text{ at constant elution volume } v_e.$$

$[\eta]^*$ is the viscosity of the linear PE of molecular mass M^* at the same elution volume

$$([\eta]^* = kM^{*a})$$

		g'_n			
No.	Fr.	1	5	9	calcul.
6		0.38	0.475	0.45	0.43
8		0.39	0.47	0.38	0.50
10		0.52	0.47	0.39	0.52
12		0.42	0.49	0.42	0.54
14		0.41	0.65	0.54	0.60
16		0.64	0.45	0.60	0.63

$g'_{n \text{ calc.}}$ is obtained by using $k = 7 \times 10^{-4}$ and $a = 0.67$ and the M^* and $[\eta]_b$ average values.

Table 8. g' can be determined from the viscosity and GPC data by using this relation established with constant elution volume.

$$g'_n = \{ [\eta]_b / [\eta]_l^{v_e} \}^{1+a}$$

Here a is the parameter of the Mark-Houwink relation. In Table 8, one can see the g' values given by three laboratories as well as g' calculated by considering the average values given in the preceding tables.

The conclusions relating to the g' parameter are very similar to those of the M_w determination. It should be noted that the g'_n parameter decreases when the molecular weight increases. The fractions of low molecular weight are less branched.

After this study on the LDPE fractions, we have again examined the unfractionated LDPE B sample. For this sample, the results are very different, as shown in Table 9. This table gives the viscosity, osmometry, light scattering and GPC data. For the viscosity measurements, the determination of M_n by GPC and osmometry and for M_w by light scattering, the results are in good agreement from one measurement to another and especially the results of M_w by light scattering are noteworthy.

But the results for apparent M_w by GPC present some dispersion and the two values (M_w)* which are corrected for the long-chain branching are not consistent with the light scattering data. The GPC values are always lower than the values determined by light scattering.

* Values given in parentheses in Table 9.

Table 9. Molecular parameters of whole sample LDPE B (the values in parentheses are corrected for long-chain branching)

	η	M_n		M_w	
		Osm.	GPC (app M_n)	LS	GPC (app M_w)
2	0.79		15 500		73 000
3	0.85		12 000 (20 000)		113 000 (321 000)
4	0.82	24 000	16 400	$\left\{ \begin{array}{l} 540\,000 \\ 515\,000 \\ 560\,000 \end{array} \right.$	110 000
5			14 000 (20 000)		140 000 (190 000)
8	0.90			$\left\{ \begin{array}{l} 550\,000 \\ 660\,000 \end{array} \right.$	
9	0.86		13 000		158 000
10	0.90		13 600		117 000
11		22 000		530 000 505 000	

These latter results emphasize the ever-present difficulty of obtaining a good value for M_w by GPC when using a branched sample with a very large molecular weight distribution. One can try to explain this fact by considering:

- (1) The difficulty of evaluating exactly the contribution to M_w of the fraction of very high molecular weight which is present in very small quantity;
- (2) The problem of the calibration of the curve of $\log M$ or $\log([\eta]M)$ versus v_e in the high molecular weight range.

We have already noted that the branching index g'_n obtained on the fractions of LDPE sample B is a function of M_w . In the case of unfractionated polymer (whole polymer), it is possible to characterize the distribution of the branching index g'_n by plotting the viscosity $[\eta]_i$ of each fraction from GPC as a function of the corresponding elution volume $v_{e,i}$ for the linear polyethylenes and the branched polyethylene sample. But, in order to have more accurate values of g'_n by combining GPC and viscosity measurements, one correction due to the axial dispersion of the columns is necessary⁵. This problem of the correction has actually been studied by the participants of the Working Party.

CONCLUSION

To conclude this analysis of all the results, the following conclusions may be drawn:

The agreement for the $[\eta]$ values is relatively good for all the samples; the precision is about ten per cent.

The agreement between the M_n values obtained by osmometry and by GPC is also satisfactory.

The M_w values by light scattering are consistent for the unfractionated

HDPE and LDPE B but for the LDPE B fractions, the dispersion is much larger.

The results by GPC (for M_n and M_w) are consistent for the HDPE and also for the LDPE B fractions. In particular, there is relatively good agreement between the M_w values from light scattering and those from GPC.

The situation for the LDPE of broad molecular weight distribution is different. If the apparent M_w values (obtained by GPC from the calibration curve $\log M$ versus elution volume v_e established for linear polymer) are consistent, the determination of M_w is not good, because after correction of the long chain branching effect by using for instance the universal calibration curve $\log([\eta]M)$ versus v_e , the M_w is always lower than M_w obtained by light scattering.

Finally it seems to be necessary to continue this work in order to study the problem of the determination of the M_w and the distribution of the branching by GPC for the unfractionated LDPE samples. For this, it has been decided to study the LDPE sample C and also two branched PE which are less polydisperse.

We want to express here our thanks to the laboratories which participated in the programme undertaken in the framework of the Division of Macromolecular Chemistry of IUPAC.

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