

# MOLECULAR CHARACTERIZATION OF COMMERCIAL POLYMERS

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## ABSTRACT

In the frame of the activities of IUPAC Macromolecular Division, samples of different commercial polymers have been sent to different laboratories in order to measure their molecular properties; molecular weights, molecular weights distribution, viscosity index, degree of branching and stereoregularity.

The purpose of this work was to compare results obtained in different locations, not as it was done before on well defined monodisperse systems but on samples with broad distribution and in some cases branches.

This report is a summary of the result collected on polystyrene, polyvinylchloride, low and high density polyethylene. It shows that there is a good agreement on viscosity values for all the samples. As for molecular weights, the agreement is good for polyvinylchloride, less good for polystyrene and very poor for polyethylene. Some explanations are proposed for these discrepancies but further work must be done in order to obtain better results.

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Two years ago the Division of Macromolecular Chemistry of the IUPAC decided to have a study made of a certain number of samples by laboratories which specialize in the characterization of polymers. The two main reasons for the study were:

- (1) It was essential to see if the same techniques used in different laboratories led to the same results;
- (2) It was interesting to compare different methods and to see if they led to similar conclusions and if, from this fact, one obtained precise information on certain characteristics of these samples (molecular parameters, degree of branching, stereoregularity, etc. . . .).

After discussions within the framework of the Division of Macromolecular Chemistry as well as within the framework of the Working Party on 'The Relationship of Performance Characteristics to Basic Parameters of Polymers' organized by Dr Barrett, it seemed to us preferable to carry out this study on commercial samples rather than on samples prepared under optimum conditions, that is as monodispersed as possible and not presenting ramifications. This decision was made in order to have conditions similar to those which industrial laboratories have to face, and to allow comparison of the measurements of polydispersity. Besides a similar study had already been undertaken by the IUPAC a few years ago on monodispersed samples of polystyrene<sup>1</sup>; we thought, therefore, that recent technical improvements might allow more complex problems to be solved.

**(A) SAMPLES AND EXPERIMENTAL TECHNIQUES**

The study dealt with four types of samples:

- A. A sample of polystyrene (PS Lustrex) prepared by Monsanto Chemicals—36 laboratories sent more or less complete results.
- B. A sample of polyvinyl chloride (PVC Solvic) made by Solvay which was studied by 22 laboratories.
- C. A sample of polyvinyl acetate (PVAc) made by Hoechst, and studied by a restricted number of laboratories, 12.
- D. A series of polyethylene (PE) samples comprising three samples of low density (LDPE) prepared by BASF and two samples of high density (HDPE) made by Dow Chemicals. These samples were studied by about 15 laboratories.

It must be noted that a hundred laboratories had asked for samples and we obtained results from only 47 laboratories. The list of these laboratories is given in an appendix which also indicates the samples studied by these laboratories and the experimental techniques which they used.

Effectively the participants had complete freedom of choice as to the methods used and the experimental conditions. They were asked to specify in their report not only their methods but also the solvents used, the concentrations and the temperatures at which these measurements had been made.

The essential part of the results concerns the determination of the molecular parameters, namely:

1. *Intrinsic viscosities*: obtained from capillary viscometer data, the most popular instrument being the Ubbelohde suspended level viscometer.
2. *Molecular weight averages*: for these, four techniques were used, mainly:
  - (a) osmotic pressure measurements (Osm.) by automatic membrane osmometers (Mechrolab, Hallikainen, Melabs, etc.) and ebulliometry or vapour pressure (VPO) studies in the case of the polyethylenes.
  - (b) light scattering (LS) studies using the Brice Phoenix, the Sofica, the Shimadzu, or other less widely known instruments.

Table 1. Results of the viscosity measurements for polystyrene (PS Lustrex)

Experimental conditions	[ $\eta$ ] dl/g			$k'$	
	$N$	$\langle[\eta]\rangle_{av}$	Extreme values	$N$	$k'$
Toluene 25°	9	0.773	0.735–0.862	3	0.31–0.32–0.326
Toluene 30°	1	0.69		1	0.8
Toluene 40°	1	0.712			
Benzene 20°	1	0.86			
Benzene 25°	8	0.789	0.755–0.820	3	0.30–0.31–0.404
Benzene 30°	1	0.899			
THF 23°	1	0.75		1	0.5
THF 25°	2	0.776	0.769–0.784		
THF 30°	1	0.75		1	0.4
Cyclohexanone 30°	1	0.766			
Butanone 25°	3	0.444	0.438–0.450	3	0.385–0.40–0.53
Butanone 30°	1	0.41		1	0.7
Cyclohexane 35°	3	0.369	0.353–0.379		

- (c) ultracentrifugation (UC) determinations either by sedimentation rate measurements or by sedimentation equilibrium.
- (d) gel permeation chromatography (GPC) studies. Certain authors used their GPC results to determine from a standardization curve and by integration the different averages of the molecular weights.
3. *Distribution of molecular weights*: the distribution curves were obtained with the aid of four techniques—gel permeation chromatography, Baker and William type column fractionation, successive precipitation and ultracentrifugation (determination of  $g(s)$ ).
- Finally, as regards structural parameters, we have had submitted a certain number of results obtained by completely different techniques such as infra-red (i.r.), nuclear magnetic resonance (n.m.r.), etc. These studies were carried out on PVC and especially on the polyethylenes.

## (B) ANALYSIS OF THE RESULTS

### I. Polystyrene study

This polymer being one of the most classic and most easy to handle, we were hoping that excellent agreement would be obtained. This is rather far from being the case.

Considering the important mass of results which we have examined, it was impossible to report them all here in detail. We have therefore gathered together in the tables the facts which seemed to us worthy of interest.

*Table 1* gathers together the results obtained by viscosity measurements. This table shows the nature of the solvent, the temperature of the measurement, the average value when there were several results ( $N$  indicating the number of measurements made) and the extreme values. These latter are not very significant because in many cases the results group well except for one or two aberrant measurements.

The whole of these results is, in our opinion, very satisfactory. Let us take as an example the case of benzene at  $25^\circ$  for which there were eight measurements. The average value is 0.789 decilitre/gramme, the extremes being 0.755 and 0.820, which means that they are all within four per cent of the mean value.

It is reassuring to obtain the lowest value for the  $\theta$  solvent, that is 0.369 decilitre/gramme for cyclohexane at  $35^\circ$ .

The precision of these results is rather remarkable because it is not a case of direct experimental values but of values extrapolated to zero concentration. It seems then contrary to what had been stated many times, that the method of extrapolation to zero concentration is of particular importance. This precision is not, however, sufficient to compare validly the results obtained in a like solvent at different temperatures by different experimenters.

We have also shown in this table the values of  $k'$  (Huggins constant) when the participants had calculated it. The spread of results is considerably greater and there are two aberrant points. This indicates that all the interpretations given to the coefficient  $k'$  must take account of this lack of precision.

It is current practice to calculate the viscometric average molecular weight

by using the values of the parameters  $K$  and  $a$  from the formula of Mark, Houwink and Sakurada

$$[\eta] = KM^a$$

This has been done in general by using the values of  $K$  and  $a$  in the *Polymer Handbook*<sup>2</sup>, and leads to the value

$$M_v = 200\,000 \pm 12\%$$

The extreme molecular weights thus obtained are 183 000 and 228 000.

*Measurement of the different molecular weight averages*

As in the case of the intrinsic viscosity, we have brought together the results of the different molecular weight averages in *Table 2* on which we now comment.

(a) *Number average molecular weight*—As the study of the distribution of molecular weights will show, the polymer studied was very polydispersed and because of this it had an appreciable percentage of molecules of low molecular weight.

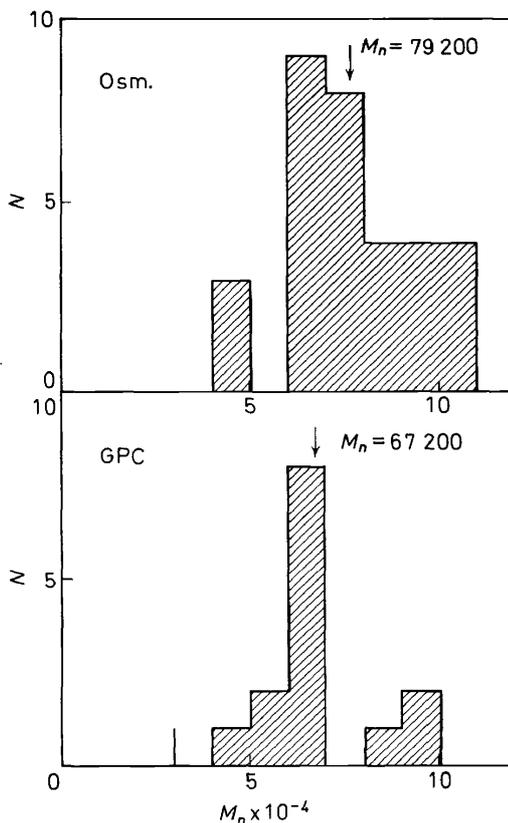


Figure 1. Histograms of the number average molecular weights,  $M_n$ , for polystyrene measured by osmometry and by GPC ( $\Delta M = 10\,000$ ).

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The experimenters who did take account of this fact and who used too porous membranes had difficulties because some of the polymer diffused into the solvent compartment. This explains clearly the dispersion of the results and the fact that  $M_n$  varies from 42000 to 110000. Besides although according to the producer it was a sample free from additive or stabilizer, two laboratories, the Charles University in Prague and the C.R.M. in Strasbourg, found in the last fraction a not negligible percentage of substances which were not polystyrene. One is tempted, since the diffusion of the small masses through the membrane leads to too high a value for  $M_n$ , to give more credibility to the low values. *Figure 1* gives a histogram of the results distributed in  $\Delta M$  sections of 10000 and it seems that a value of the order of 70000 may be the most reasonable.

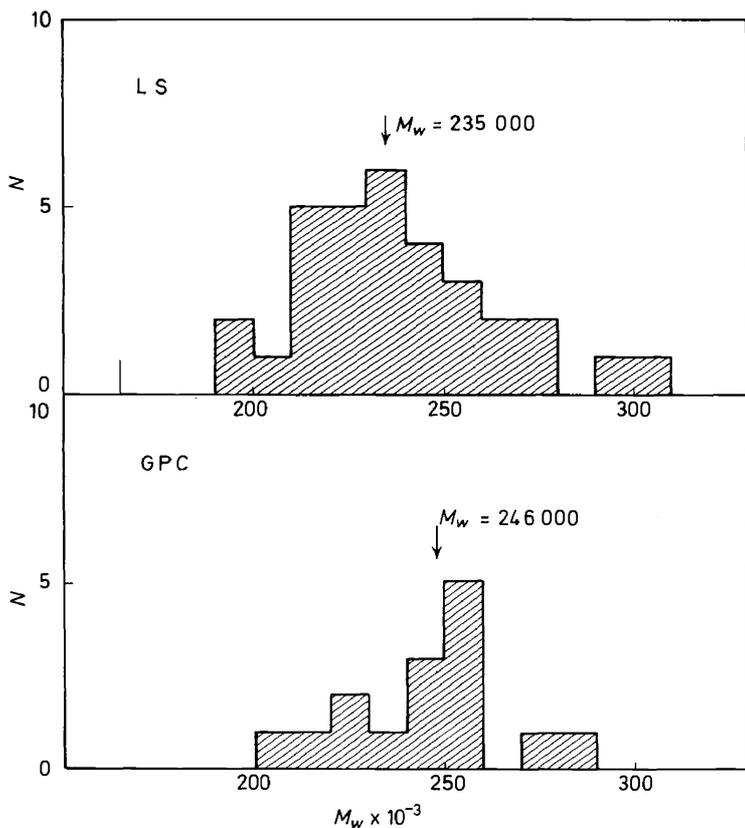


Figure 2. Histograms of the weight average molecular weights,  $M_w$ , for polystyrene measured by light scattering and GPC ( $\Delta M = 10000$ ).

The results of the number averages measured by GPC present a reasonable average value but a great scatter. This doubtless comes from the difficulty of measuring small quantities of polymer of low molecular weight. For comparison we have presented the histogram of the GPC results in order

to compare it with that obtained from the osmotic pressure studies (see *Figure 1*).

(b) *Weight average molecular weights*—The dispersion of the results obtained from light scattering determinations is rather surprising (see *Figure 2*). As this technique is now a classic one and polystyrene is one of the easiest polymers to study, it would have been normal not to have had a dispersion of more than  $\pm 10$  per cent. Here it reaches  $\pm 30$  per cent which is difficult to explain. We have tried to see if there were correlations between the experimental procedure and the results obtained but have not been able to find any and neither the different values of  $dn/dc$  used, nor the initial concentrations, nor the apparatus and the calibration used, allow an explanation of this result.

The only interpretation which does not put in question the practice of this technique would be to assume, in spite of the affirmation of the producer, that the product was heterogeneous and that the samples supplied to the different laboratories differed notably one from another. This does not seem very probable because the viscosity measurements led to very reproducible results and one cannot see why heterogeneities in the sample should keep  $[\eta]$  constant and cause  $M_w$  to vary.

Table 2. Molecular weights and degree of polydispersity of the polystyrene (PS Lustrex)

Molecular parameters	<i>N</i>	Average value	Extreme values
$M_n$ GPC	15	67 250	30 000–98 000
$M_n$ Osm.	32	79 200	41 700–108 000
$M_v$ Visc.	18	200 000	183 000–228 000
$M_w$ GPC	15	246 000	208 000–289 000
$M_w$ LS	33	235 000	165 000–302 000
$M_w$ UC	10	217 000	173 000–247 000
$M_z$ GPC	6	486 000	427 000–557 000
$M_z$ UC	6	397 000	310 000–451 000
dP GPC	15	3.89	2.64–7.2
dP $M_w$ LS/ $M_n$ Osm.	17	3.22	2.20–4.88
dP Fract.	6	3.06	2.40–3.55

It is currently admitted that the measurement of  $M_w$  by GPC is much more precise than that of  $M_n$ . That is partially true in this case but the precision is far from being as good as one would have expected (*Table 2* and *Figure 2*). This is astonishing, especially in the case of polystyrene because the standardization of the columns was carried out on polystyrene samples supplied in most of the cases by the firm Waters. Can it be that the dispersion of the GPC result only reflects the dispersion of the light scattering results? Since the standardization curve is constructed from masses measured by light scattering it is not surprising that the precision obtained by this technique was not superior to that which one obtains on standards. It seems, however, that there are small molecules contained in the sample whose presence shows itself by a very small difference between the curve and the baseline, which are at the origin of these deviations. To confirm this point a measurement on a less polydispersed sample would appear essential.

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We shall not discuss at length the results of sedimentation. The values are reasonably grouped and agree largely with those of GPC and light scattering.

If, in terms of all these results one had to propose a value of  $M_w$  for this sample, we think that we would quote 230000 to within about 10 per cent.

There is nothing to say on  $M_z$ ; the precision of its determination is rather low. It is curious to notice that by GPC one obtains clearly overestimated values. Many authors have not calculated this parameter from their diagrams.

In view of all these results it seems that the degree of polydispersity, that is, the quantity  $dP = M_w/M_n$  is of the order of 3.4. There also the dispersion of the results is great even when the authors have carried out a careful fractionation. Indeed by this latter technique, which is the most precise in our opinion, one finds values of  $dP$  varying between 2.40 and 3.55. It is possible that the dispersion of the values obtained by GPC is tied to the fact that the experimenters did not use columns having a power of resolution sufficiently large in the region of low molecular weights. Let us note, however, that the GPC results are better than the study of the table allows one to

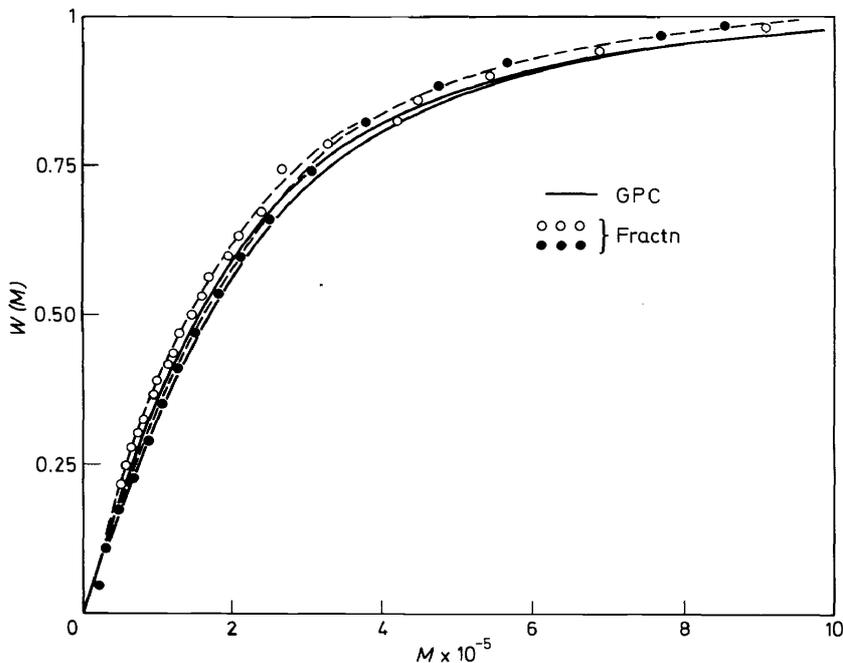


Figure 3. Integral distribution curves of the molecular weights ( $M_w$ ) for polystyrene.

suppose because with the exception of the two extreme values cited, all the results are included between 3.15 and 4.30. The authors who make a correction to take account of the power of resolution of the instrument slightly reduce the too high values of  $dP$ , but this correction is largely lower than experimental errors.

*Molecular weight distribution curves*

As in the majority of cases, the distribution curves of molecular weights have not been calculated from all the GPC results, we have compared only the data supplied by four laboratories namely the Charles University in Prague (GPC and column fractionation), the Shell Laboratory in Amsterdam (GPC), Montecatini Edison (fractionation) and the C.R.M., Strasbourg (GPC and fractionation). The results are represented as cumulative weight fractions in *Figure 3* and show a very satisfactory agreement. The agreement is less good for the results obtained by classical fractional precipitation which shows the reason for the interest in fractionating columns.

*Other parameters*

Certain authors gave the values of the radius of gyration in methylethyl ketone, where it is of the order of 170 Å, that is, too low to have an acceptable precision. In benzene at 25° one has as values: 500–420–280 and 170 Å,

Table 3. Values of the second virial coefficient,  $A_2$ , for polystyrene (PS Lustrex)

Solvent		$A_2 \times 10^4(\text{cgs})$
Toluene 25°	Osm.	5.7
	LS	4.75–8–10
Benzene 25°	Osm.	6.03
	LS	4.20–4.7–5.04–5.37
Butanone 25°	Osm.	0.76
	LS	1.11–1.5–3.75

the dispersion is considerable. The values of the virial coefficient  $A_2$ , either by osmometry or by light scattering, are better; some results are gathered together in *Table 3*.

**II. Polyvinyl chloride study**

Contrary to what one would believe, given the well-known difficulties of dissolving this polymer, the results obtained are better than those which we have just reported on polystyrene.

Only two solvents lead to satisfactory results: cyclohexanone and tetrahydrofuran (THF). Measurements made in other solvents (dioxan, dimethyl formamide, butanone) led to aberrant results for  $M_w$  which we have left out of this report.

*Table 4* gives the values of limiting viscosity number and of the Huggins constant. *Table 5* gives the values of the molecular weights, the degree of polydispersity obtained by different techniques and also the extreme values (a value in parentheses means that it is a case of a unique measurement very different from the average values obtained by the whole of the experimenters).

*Figure 4* shows the histogram ( $M_n$  and  $M_w$ ) corresponding to the different techniques. Agreement is satisfactory. We would not have expected any better agreement, especially as many GPC curves were calculated from a

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standardization of the method carried out with polystyrene samples. The change to polyvinyl chloride was carried out in the majority of cases using the method recommended by the manufacturer<sup>3</sup>. This method seems inexact to us<sup>4</sup>, but by chance it has led to good results on this PVC sample.

It was also possible to compare the distribution curves obtained by GPC and by sedimentation rate by using the relationship  $S = k'M^{a\ddagger}$ . The results

Table 4. Results of viscosity measurements for polyvinyl chloride (PVC Solvic)

Experimental conditions	[ $\eta$ ]dl/g			$k'$	
	$N$	$([\eta])_{av.}$	Extreme values	$N$	$k'$
Cyclohexanone 25°	9	0.81	0.72 -0.907	5	0.375-0.31-0.30 0.29-0.72
Cyclohexanone 30°	1	0.88			
THF 25°	9	0.819	0.764-0.87	3	0.37-0.44-0.36

Table 5. Molecular weights and degree of polydispersity of polyvinyl chloride (PVC Solvic)

Molecular parameters	$N$	Average value	Extreme values
$M_n$ GPC	{ 12	36 700	29 600-46 000
	{ 13	39 300	29 600-(70 000)
$M_n$ Osm.	16	38 600	(24 800)- 53 000
$M_v$ Visc.	9	64 600	(45 700)- 71 000
$M_w$ GPC	{ 12	79 350	69 000- 97 000
	{ 13	83 700	69 000-(136 000)
$M_w$ LS	15	84 000	60 200-102 000
$M_w$ UC	2	94 000-100 000	
$M_z$ GPC	5	136 800	110 000-170 000
$M_z$ UC	1	154 000	
dP GPC	13	2.17	(1.68 <sub>s</sub> )-2.50
dP $M_w$ LS/ $M_n$ Osm.	10	2.22	1.82-2.90
dP UC	2	2.2-2.85	

are presented in Figure 5. *A priori*, they appear less satisfactory than for polystyrene, but it must not be forgotten that the molecular weight scales differ by a factor of two. It seems, therefore, that the disagreement comes solely from a difference in the methods used by the authors for determination of the molecular weights.

Regarding the values of  $A_2$ , the scatter is rather small and one obtains in THF:  $A_2 = 1.2 \times 10^{-3}$  to almost 20 per cent, in cyclohexanone:  $A_2 = 1.7 \times 10^{-3}$  to almost 10 per cent. Certain authors determined the radius of gyration. They obtained values which in our opinion are inexact, especially in cyclohexanone, because the molecular weight of this sample is too low for it to have a radius of gyration measurable by light scattering. Three results of tacticity measurements by n.m.r. were provided. They are very close and allow one to give a degree of syndiotacticity of the order of 55 per cent.

† Data from Koninklijke/Shell Laboratorium, Amsterdam.

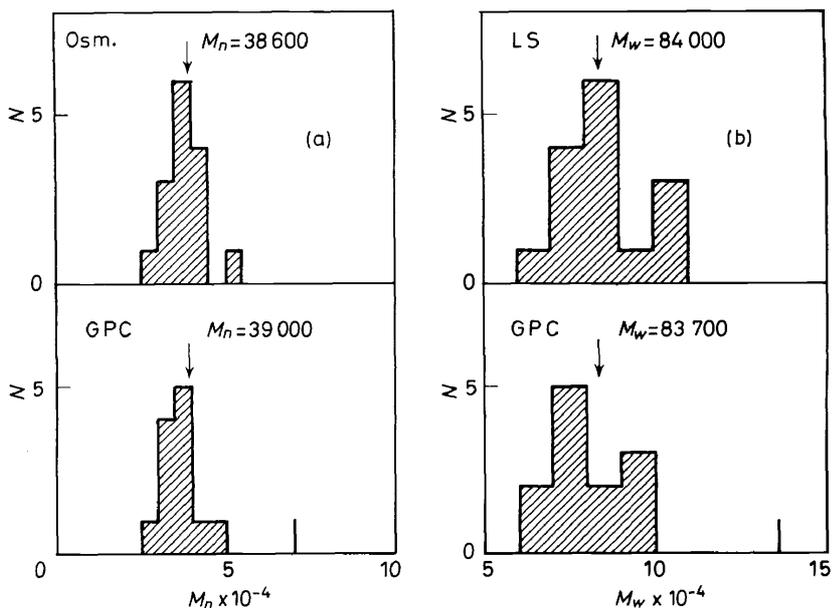


Figure 4. Histograms of the molecular weights: (a)  $M_n$  (osmometry-GPC) and (b)  $M_w$  (LS-GPC) for polyvinyl chloride ( $\Delta M = 5000$  for  $M_n$ ;  $\Delta M = 10000$  for  $M_w$ ).

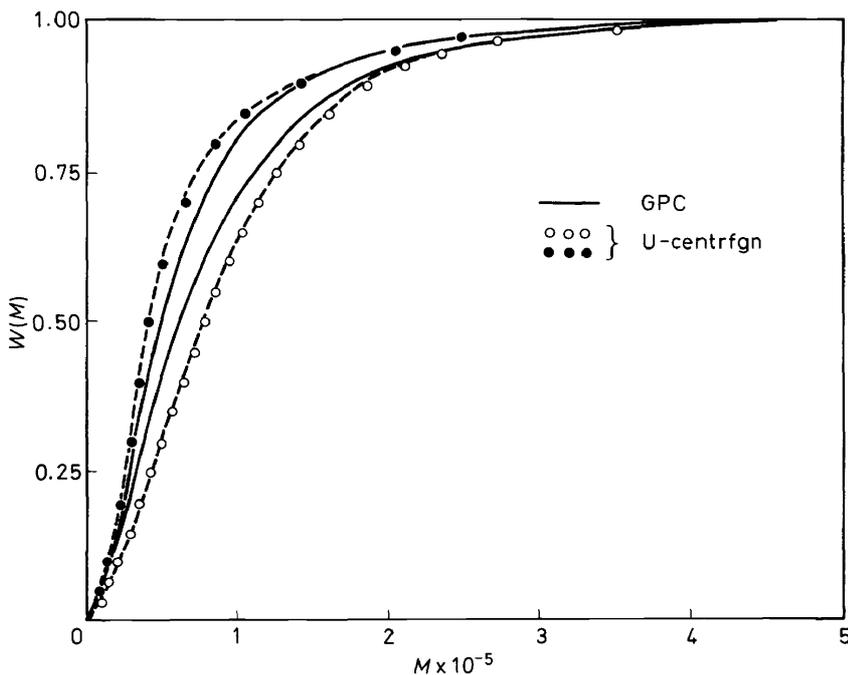


Figure 5. Integral distribution curves of the molecular weights ( $M_w$ ) for polyvinyl chloride (— GPC; - - - ultracentrifugation; ●:  $\alpha' = 0.7$ , ○:  $\alpha' = 0.5$ ).

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One author† determined the short chain branching ratio (4 CH<sub>3</sub> for 1000 CH<sub>2</sub> total). One can also cite the determination of unsaturation (1.76 —CH=CH— groups ~ 0.06 vinyl and vinylidene groups per 1000 C total).

Finally there seem to be two reasons to explain the better agreement obtained on this sample than on the polystyrene:

(1) Only the laboratories having experience in the area of measurement of molecular weight of PVC in dilute solution tackled this problem.

(2) It was a case of a relatively monodispersed sample ( $dP \sim 2.2$ ), and therefore easier to measure.

### III. Study of polyvinyl acetate

We were hoping when distributing this sample to obtain information on the degree of branching so as to be able to compare the values of the branching indices obtained by different laboratories. However, this was not possible

Table 6. Viscosity, molecular weights and degree of polydispersity of polyvinyl acetate (PVAc Hoechst)

Molecular parameters	N	Average value	Extreme values	
[ $\eta$ ] dl/g	Butanone 25°	3	0.684	0.64–0.72
	THF 25°	2	0.723–0.73	
	THF 30°	1	0.747	
	Benzene 25°	1	0.72	
	Acetone 25°	1	0.73	
—Methanol 25°	1	0.362		
$M_n$ GPC	6	52 400	40 000–63 600	
$M_n$ Osm.	12	78 400	50 000–112 000	
$M_v$ Visc.	6	196 000	137 000–331 000	
$M_w$ GPC	6	233 500	202 000–263 000	
$M_w$ LS	13	301 300	220 000–392 000	
$M_w$ UC	1	243 000		
$dP$ (3 methods)	19	4.29	3.55–5.08 (2.17–7.56)	

as only one laboratory‡ studied this problem. Also in view of the small number of measurements (limiting viscosity number and molecular weights) carried out on this polymer, it is impossible for us to give a worthwhile analysis of the results obtained, which are summarized in Table 6.

### IV. Study of the polyethylenes

This was the most difficult problem because this polymer is soluble only at high temperature and has a tendency to maintain the highly stable crystal nuclei. As in the other cases, we have gathered together in four tables the results of viscosity measurements (Tables 7 and 8) and the measurements of molecular weights (Tables 9 and 10).

If the experimental scatter of the results of the limiting viscosity numbers is relatively small, the same is not true for the molecular weights which are shown in Tables 9 and 10. (See also Figures 6, 7, 8 and 9). In fact, it was noted that the agreement between the values of  $M_n$  obtained by GPC, osmometry

† Date from Solvay. ‡ C. R. M., Strasbourg.

or ebulliometry is remarkably good for the 'high density' polyethylenes (HDPE); it is less good but still acceptable for the low density material (LDPE).

On the other hand the variations which one observes for the weight average molecular weights are considerable. Let us examine first the results obtained with the high density polyethylenes (HDPE) considered to be linear. GPC like light scattering gives values fairly well grouped for the NMWD sample and there is acceptable agreement between the two techniques. In the case of the BMWD sample, the dispersion of the values obtained by GPC is rather surprising because there are values between 130000 and 400000 distributed uniformly on the histogram. This seems inexplicable to us because the same experimenters studied both these samples. Can it be due to the fact that the second sample is more polydispersed? This is a point which would be worth a more detailed study.

The results on the low density polyethylenes are rather remarkable because there is no correspondence between the measurements of  $M_w$ , obtained either by GPC or by light scattering. The values by GPC are systematically lower than the values obtained by light scattering. This is easily explained if the experimenters used for their standardization the curve traced from linear polyethylene. Indeed for equal weight a branched polymer has a smaller dimension than the corresponding linear one and will be eluted, therefore, like a smaller polymer. Certain authors, to avoid this error, have either used the standardization curves established for branched polyethy-

Table 7. Results of viscosity measurements for the samples of high density polyethylene HDPE/ NMWD and HDPE/BMWD

Experimental conditions	N	[ $\eta$ ] dl/g	
		NMWD	BMWD
Decalin 130°	1	1.31	2.30
Decalin 135°	4	1.75 $\pm$ 3%	2.18 $\pm$ 7%
Tetralin 130°	1	0.98	1.80
Dichlorobenzene 135°	1	0.98	1.77
Trichlorobenzene 130°	1	1.02	1.83
$\alpha$ -Chloronaphthalene 125°	1	0.81 <sub>5</sub>	1.44
<i>p</i> -Xylene 105°	1	0.97	1.77

Table 8. Results of viscosity measurements for samples of low density polyethylene: LDPE A, B and C

Experimental conditions	N	[ $\eta$ ] dl/g			
		A	B	C	%
Decalin 135°	4	1.03	1.03	1.04 <sub>3</sub>	$\pm$ 10%
Decalin 130°	1	1.1	1.12	1.08	
Dichlorobenzene 135°	1	0.87	0.88	0.83	
Trichlorobenzene 135°	1	0.903	0.913	0.888	
Trichlorobenzene 130°	1	0.902	0.931	0.896	
$\alpha$ -Chloronaphthalene 125°	1	0.686	0.693	0.693	
<i>p</i> -Xylene 81°	1	0.98	1.03	0.94	
<i>p</i> -Xylene 105°	1	0.89	0.87	0.89	

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Table 9. Molecular weights and degree of polydispersity of the samples of high density polyethylene HDPE/NMWD and HDPE/BMWD

Molecular parameters	<i>N</i>	Average value	Extreme values	
$M_n$ GPC	NMWD	14	20800	10600–49500
	BMWD	12	13900	9900–28000
$M_n$ Osm.	NMWD	10	20400	13600–37730
	BMWD	9	13800	8200–24000
$M_w$ GPC	NMWD	14	87600	36620–186000
	BMWD	12	250250	131000–385000
$M_w$ LS	NMWD	5	57160	51300–76000
	BMWD	5	146800	80000–200000
<i>dP</i> GPC	NMWD	14	3.84	2.85–7.9
	BMWD	12	19.80	10.9–30.9
<i>dP</i> LS/Osm.	NMWD	4	2.75	2.35–3.17
	BMWD	4	11.6	8.2–17.6
<i>dP</i> fract.	NMWD	2	2.3	2.2–2.4
	BMWD	2	9.6	7.15–12.1

Table 10. Molecular weights of the low density polyethylenes LDPE A, B and C

Molecular parameters	<i>N</i>	Average value	Extreme values	
$M_n$ GPC	A	5	16250	13740–18400
	B	4	16350	15400–17400
	C	4	16280	15700–17100
$M_n$ Osm. or ebul.	A	9	21930	12350–27700
	B	9	20870	14000–27500
	C	9	21150	12000–31600
$M_w$ GPC	A	4	247000	88700–414800
	B	4	302000	102000–492900
	C	4	244000	92000–448200
$M_w$ LS	A	9	$2.30 \times 10^6$	785000– $>6 \times 10^6$
	B	8	584000	425000–730000
	C	8	$1.02 \times 10^6$	425000– $1.6 \times 10^6$

Table 11. Analysis of the short chain branching and unsaturation by i.r. for the low density polyethylenes (LDPE) and high density polyethylenes (HDPE)

Groups analysed	HDPE		LDPE		
	NMWD	BMWD	A	B	C
Methyls/100C	~0.1 (0–0.14)	~0.14 (0–0.27)	2.93 (1.6–4.7)	2.83 (1.45–4.7)	2.83 (1.5–4.9)
Vinyls/1000C	0.67 (0.35–1.71)	1.46 (0.52–1.90)	0.12 (0.06–0.2)	0.18 (0.11–0.24)	0.11 (0.05–0.17)
Vinylidenes/1000C	~0.03	~0.04	0.39 (0.31–0.54)	0.32 (0.21–0.46)	0.39 (0.29–0.61)
<i>trans</i> —CH=CH—/1000C	~0.02	~0.02	~0.08	~0.08	~0.08

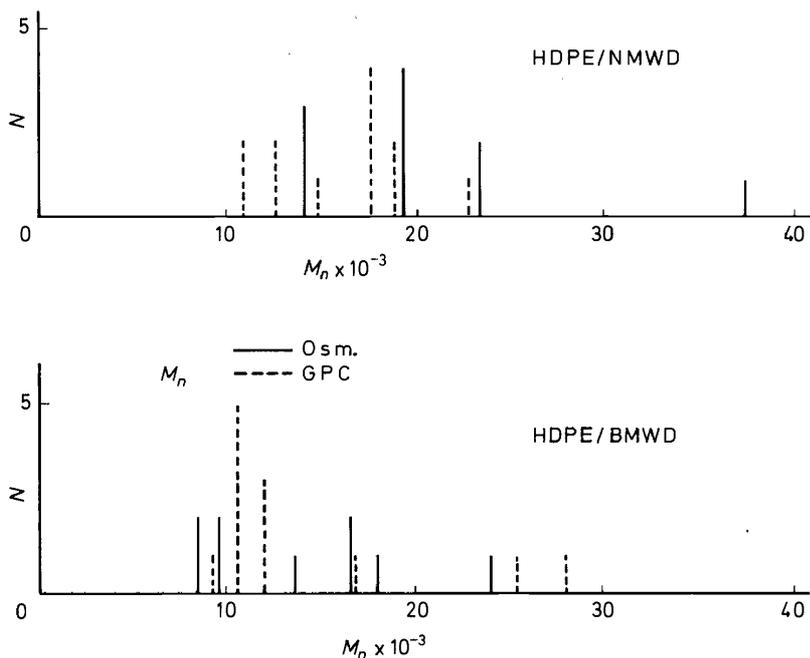


Figure 6. Histogram of the molecular weight  $M_n$  (osmometry-GPC) for the two samples of 'high density' polyethylene: HDPE/NMWD and HDPE/BMWD ( $\Delta M = 10000$ ).

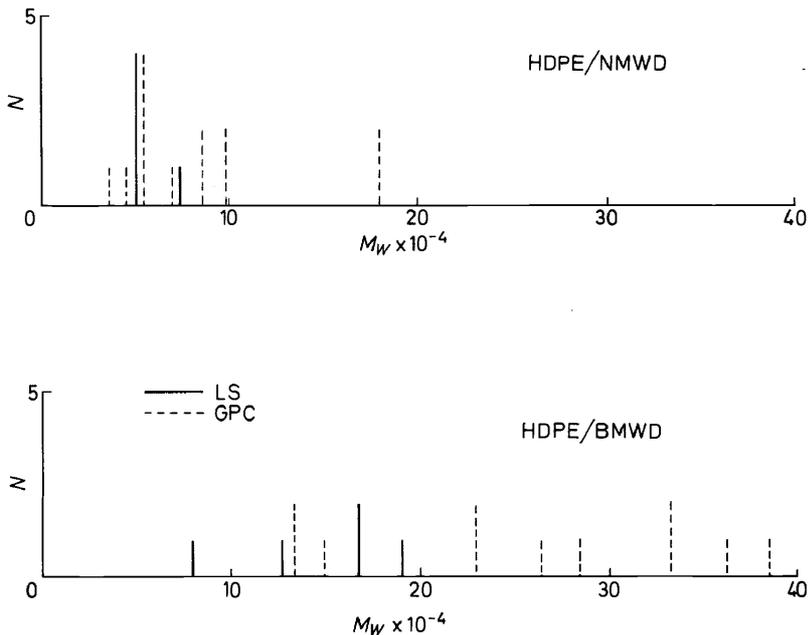


Figure 7. Histograms of the molecular weight  $M_w$  (LS-GPC) for the two samples of 'high density' polyethylene: HDPE/NMWD and HDPE/BMWD ( $\Delta M = 10000$ ).

MOLECULAR CHARACTERIZATION OF COMMERCIAL POLYMERS

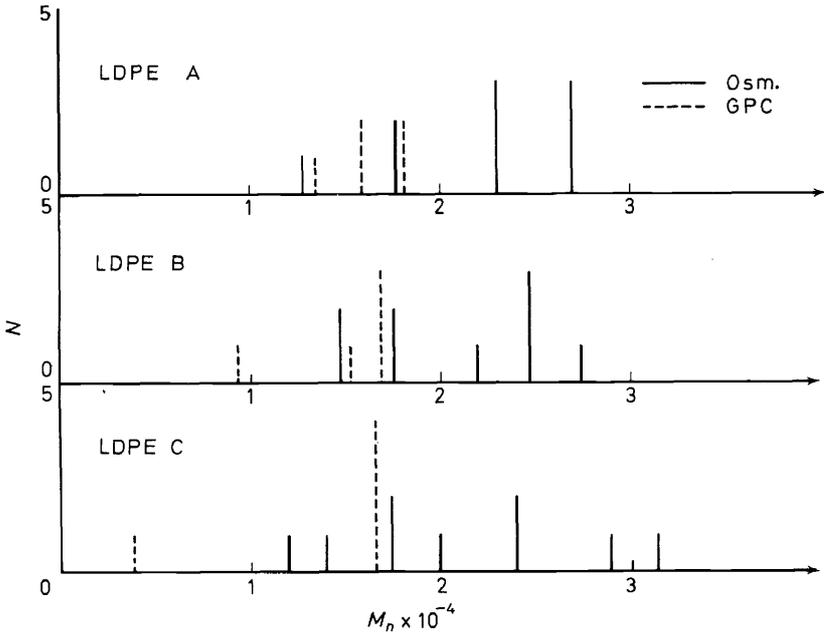


Figure 8. Histograms of the molecular weight  $M_n$  (— Osm.; - - - GPC) for the three samples of 'low density' polyethylene: LDPE A, B and C ( $\Delta M = 2000$ ).

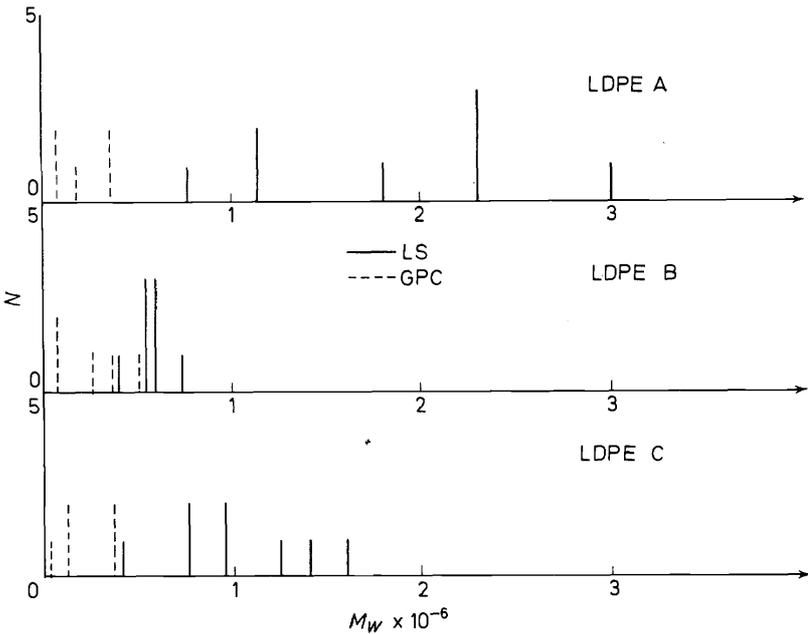


Figure 9. Histograms of the molecular weight  $M_w$  (— LS; - - - GPC) for the three samples of 'low density' polyethylene: LDPE A, B and C ( $\Delta M = 10^5$  for GPC; A:  $\Delta M = 2 \times 10^5$ , B:  $\Delta M = 2 \times 10^4$  and C:  $\Delta M = 2 \times 10^5$  for LS).

lenes or tried to take account of the branchings. It seems that all these corrections are insufficient.

In view of the heterogeneity of these results it was difficult to pursue the analysis further and to compare more particularly the degrees of polydispersity and the distribution curves.

We shall content ourselves with giving the results of infra-red analysis (and of one measurement by n.m.r. in the case of the LDPE) of the chain irregularities (short chain branches and unsaturations). The results are in general in good agreement but when the accuracy becomes too low one can only quote an order of magnitude (*Table II*). Finally, other special measurements (density or differential thermal analysis, etc.) were carried out by some laboratories, but as only isolated results were presented, discussion and comparison were not possible. These results, therefore, have not been included in this report and we apologise to the authors for this omission.

### (C) CONCLUSIONS

The results of this international work are, at first sight, rather disappointing because they are not any better than those which were obtained by Atlas and Mark in 1961 on monodispersed samples of polystyrene also distributed within the framework of the IUPAC<sup>1</sup>. It seems, however, that a too pessimistic view of the situation should not be taken as the problem which was posed presented extra difficulties since it was a question not only of polydispersed polystyrenes but of various industrial polymers having a fairly large distribution of molecular weight.

In fact, the results relating to the limiting viscosity number  $[\eta]$  are very satisfactory. Similarly for the determination of heterogeneity (short chain branches and unsaturated groups) in the polyethylenes. The only points on which agreement is far from unanimous are the measurements of molecular weights and of distribution of molecular weights, although on this last point the agreement is clearly more satisfactory. As regards the scatter of the values of number average molecular weights determined by osmometry, one can associate this with the polydispersity of the samples (especially for polystyrene) and consequently a more or less considerable diffusion of low molecular weight components through the membrane. As to the weight average molecular weights,  $M_w$ , notably the ones which are measured by light scattering, a critical study of the experimental conditions used has not enabled us to offer any one reason why certain results are clearly erroneous. It seems that the only possible explanations are either the use of a poor range of concentrations or else some inadequate graphical representations which did not enable sufficient precision to be obtained in the double extrapolation to zero concentration and angle.

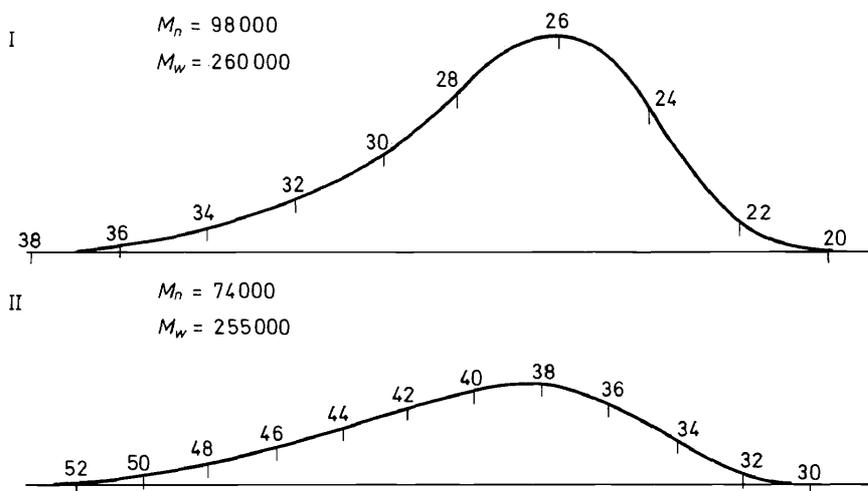
Since gel permeation chromatography is a recent technique, and since it is used here for the first time in a series of comparative experiments, we should like to discuss at greater length the problems which it poses and to show how it can be used in a more effective way to tackle the study of long chain branching.

In principle, GPC is the ideal technique to obtain rapidly, not only the different molecular weight averages, but also the complete distribution

## MOLECULAR CHARACTERIZATION OF COMMERCIAL POLYMERS

curve. In order to do this, the majority of the experimenters used a series of columns with different porosities so as to have a good selectivity over a wide molecular weight range.

This way of proceeding is not perhaps the one which always leads to the best results when dealing with relatively polydispersed samples. Indeed, it is possible in this case that one has an insufficient resolving power, either in the region of high molecular weights, or on the contrary in the region of low molecular weights. This is doubtless what occurs in the case of the polystyrene sample. This latter, in view of its high polydispersity, possessed an important quantity of low molecular weight material which did not appear when using the standard length of the columns used by the majority of the experimenters. This is confirmed by the results obtained at P  chiney-Saint-Gobain by de Vries. *Figure 10* shows the chromatograms obtained by the latter on the polystyrene sample. The first chromatogram was obtained with a standard



*Figure 10.* Influence of the choice of columns on the GPC chromatograms for the IUPAC polystyrene, Lustrex PS, according to de Vries (P  chiney-Saint-Gobain): I, 6 m column; II, 8 m column.

column length (6 m) and leads to high molecular weight values, especially for  $M_n$ . The second, on the other hand, was carried out with a length of 8 m of column chosen so as to improve the resolving power and this leads to a better value for  $M_n$ . One can see on this figure the change of shape of the chromatograms and only the second gives the more correct results, which shows the importance of a wise choice of column length.

### Influence of branchings

Another point which seems important to us to emphasize is the fundamental disagreement which exists, especially for the low density polyethylenes, between the results of light scattering and the results obtained by gel chromatography. For example, in the case of the LDPE samples, types A, B and C,

all the values obtained by GPC are lower than those obtained by light scattering. Evidently one can explain this fact by the difficulties in carrying out the correct light scattering measurements on the polyethylenes. This explanation is not entirely satisfactory and it seems that the variations observed are tied in with a systematic error due to the presence of long chain branching.

If one standardizes a GPC instrument with a series of homologous linear polymers, the points are placed in a satisfactory way on a curve which is in general a straight line over a rather large range of molecular weights.

With branched polymers the points no longer lie on this straight line but always to the right of it. By way of an example we reproduce here the results obtained in our laboratory by J. G. Zilliox<sup>5</sup> and which are relative to linear polystyrenes and star-shaped polystyrenes (*Figure 11*). One can see that if, not knowing about the existence of the branchings, one had used the stand-

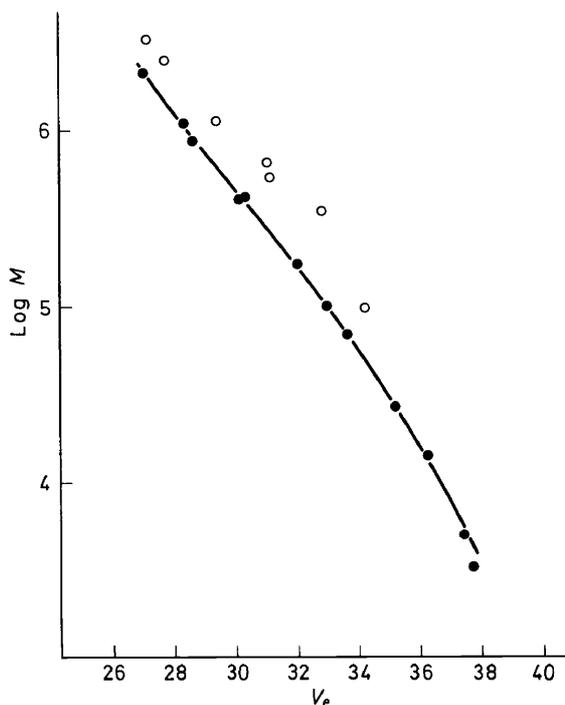


Figure 11. Standardization curve,  $\log M = f(V_e)$ , for the linear polystyrenes (●) and star (○) (After J. G. Zilliox<sup>5</sup>).

ardization curve valid in the case of linear polymers to measure the mass of the branched molecules, one would have obtained masses systematically too low as has been observed for the low density polyethylenes. Certain authors think that one can avoid this difficulty by carrying out the standardization with the help of branches fractions. This can lead to correct results only if

## MOLECULAR CHARACTERIZATION OF COMMERCIAL POLYMERS

the branched polymers form a homologous series and if the unknown samples present a branching rate identical to that of the fractions used to carry out the standardization. The chances of this happening are very low.

This difficulty, which has already been pointed out by numerous authors, should be used on the other hand to characterize branched polymers better and to allow calculation of the degree of branching more precisely.

It has been suggested that if, instead of putting only the mass as a function of the elution volume, one were to put the product of the mass by intrinsic viscosity:  $[\eta]M$ , the points would be placed on a curve called the universal curve whatever the state of branching of the samples<sup>4</sup>.

Figure 12 represents the results of J. G. Zilliox on linear and radial polystyrenes; likewise Figure 13 shows the results obtained by R. Prechner in the

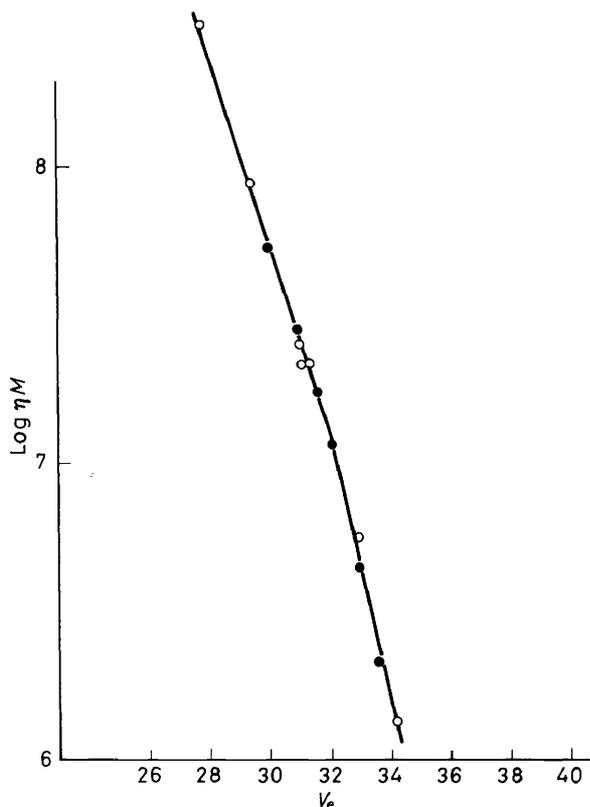


Figure 12. Universal standardization curve,  $\log \eta M = f(V_e)$ , for linear polystyrenes (●) and star (○) (After J. G. Zilliox<sup>5</sup>).

laboratories of the Société Nationale des Pétroles d'Aquitaine on three types of polymers: linear polystyrene, high density linear polyethylene and low density branched polyethylene<sup>6</sup>. All these points are placed on the same

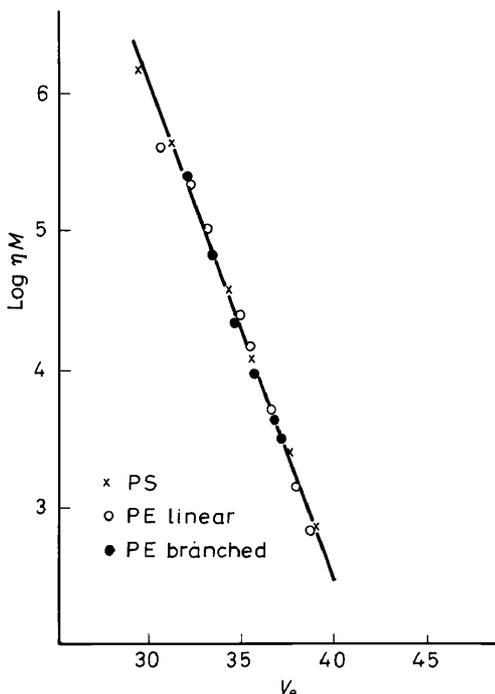


Figure 13. Universal standardization curve,  $\log \eta M = f(V_e)$ , for linear polystyrenes( $\times$ ), linear polyethylenes(O) and branched polyethylenes( $\bullet$ )(After R. Prechner<sup>6</sup>).

straight line, which comes back to saying that the elution volume is a function of the product  $[\eta]M$

$$V_e = f([\eta]M)$$

This observation will allow us to establish the relationship between the apparent mass  $M^*$  which one measures by GPC by using the standardization valid for linear polymers and the true mass of the sample. To do this, we shall assume that the viscosity relationship  $[\eta] = KM^a$  of the linear polymer is known. With this hypothesis one can easily find

$$M = M^*g'^{-1/(1+a)}$$

where  $g'$  is the classic branching index, that is, the ratio  $g' = [\eta]_{br.}/[\eta]_{lin.}$  taken at constant molecular mass. This ratio being always less than unity,  $g'^{-1/(1+a)}$  is greater than one and from this fact  $M$  must exceed  $M^*$ . If, for example, one has an index  $g'$  of 0.7 and an exponent  $a$  of the law of viscosity of 0.6, the quantity  $g'^{-1/(1+a)}$  is of the order of 1.24 which introduces a considerable error.

It is known that research on long chain branching has always been a difficult problem and that the only method which is known at present consists of measuring the factor  $g'$  which one tries to relate with the factor  $g$  representing the radius of gyration because the value of the latter is calculable

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theoretically within the framework of the Gaussian chain hypotheses. The simultaneous use of gel chromatography and of a technique like the determination of molecular weight or intrinsic viscosity which is easier to carry out, enables us to resolve this problem. Indeed, the knowledge of  $M^*$  by GPC and of  $M$  by direct measurement leads to the relationship

$$g'_M = (M^*/M)^{(1+a)}$$

Likewise, if one knows  $[\eta]^*$  and  $[\eta]$  one will have

$$g'_\eta = ([\eta]/[\eta]^*)^{(1+a)}$$

This is exact only for fractions and by way of an example we have reproduced in Table 12 the results obtained by Prechner<sup>6</sup>. The factor  $g'$  was calculated

Table 12. Branching indices  $\langle g'_\eta \rangle$  and  $\langle g'_M \rangle$  for low density polyethylene (fractions) (results according to R. Prechner<sup>6</sup>)

Fractions	$M_w \times 10^{-3}$	$\langle g'_\eta \rangle$	$\langle g'_M \rangle$
1	72.1	0.472	0.286
4	68.2	0.764	0.726
6	41.7	0.811	0.802
7	36.8	0.776	0.784
8	28.7	0.882	0.825
9	24.2	0.846	0.746
10	18.5	0.892	0.788
11	14.9	0.957	0.792
12	12	0.753	0.749

by the two methods which we have just mentioned for different fractions of low density polyethylene; one notes a rather satisfactory agreement, the small differences between the observed values being explicable by the fact that the fractions were not strictly monodisperse.

If one wishes to apply this procedure to polydisperse products, it is evident that one will obtain average values. A simple calculation shows that if  $g'$  is defined from GPC measurements and light scattering measurements  $M_w$ , one will have

$$\langle g'_M \rangle = \left( \frac{M_w^*}{M_w} \right)^{(1+a)} = \left( \frac{\sum w_i M_i g_i'^{1/(1+a)}}{\sum w_i M_i} \right)^{(1+a)}$$

where  $w_i$  represents the weight fraction of polymer mass  $M_i$  and of degree of branching  $g_i'$ .

If, instead of starting from measurements of molecular masses one uses viscosity measurements, one obtains

$$\langle g'_\eta \rangle = \left( \frac{[\eta]}{[\eta]^*} \right)^{(1+a)} = \left( \frac{\sum w_i \eta_i^* g_i'^{1/(1+a)}}{\sum w_i \eta_i^*} \right)^{(1+a)}$$

These two averages are not identical and in the case where the degree of branching increases with the molecular mass, one has

$$\langle g'_M \rangle \leq \langle g'_n \rangle$$

It seems, therefore, a good thing that these two indices  $\langle g'_n \rangle$  and  $\langle g'_M \rangle$  allow one to characterize the degree of branching of a non-fractionated sample; they have the advantage of representing purely experimental quantities whose definition does not rest on any hypothesis. It is clear that these quantities are less interesting than the values of  $g'_i$  obtained on each one of the fractions, as it is possible to do by the method of Goedhart and Opschoor<sup>7</sup>. They have, however, the advantage of being easy to determine and should, like the average molecular weights, become of current use for the determination of the degree of branching.

We would like to make a final remark on the effect of branching. This is concerned with a thermodynamic property of solutions of branched polymers, namely the lowering of their 'theta' temperature. A certain number of

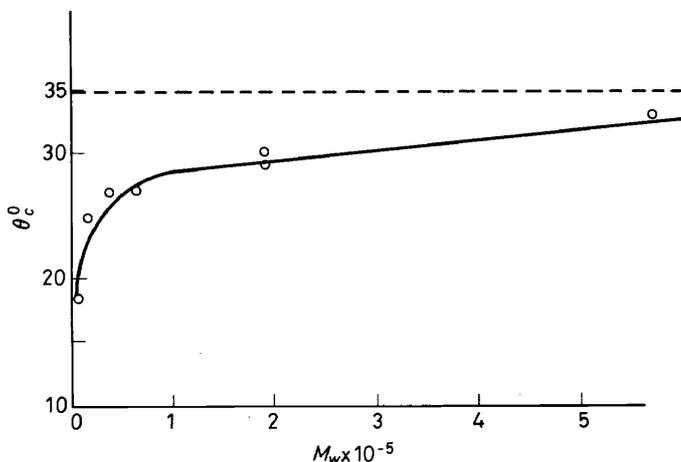


Figure 14. Variation of the  $\theta$  temperature of star polystyrenes with identical number of branches versus the molecular weight of the branch (After J. G. Zilliox<sup>5</sup>).

studies carried out in our laboratory on the  $\theta$  temperature of comb-shaped or star-shaped polystyrenes<sup>5,8</sup> have shown that in cyclohexane the temperature for which the second virial coefficient  $A_2$  becomes zero is no longer around 35° but much lower.

Figure 14 reproduces a result obtained recently by Zilliox on star-shaped polymers prepared by anionic polymerization and for which the number of branches is known. On this figure we have reported for a number of almost constant branches the variations of the  $\theta$  temperature as a function of the length of the branches of the star. One notes that, the shorter are the branches, the more the temperature is lowered, which can be explained qualitatively by saying that, in the central region of the star the segment density is raised and that because of this, the approximations made in the classical theories

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which all assume that the local concentration is low, are not valid. Some preliminary calculations made by Mme G. Candau in our laboratory seem to confirm this hypothesis, but in any case it seems here and now that there is no relationship between the factor  $g$  ratio of the radius of gyration of the branched polymer to that of the linear polymer of the same mass and this lowering of the theta point. Let us point out that this phenomenon exists also for the polyvinyl acetate sample distributed within the framework of the IUPAC programme. Figure 15 shows the variations of the second virial

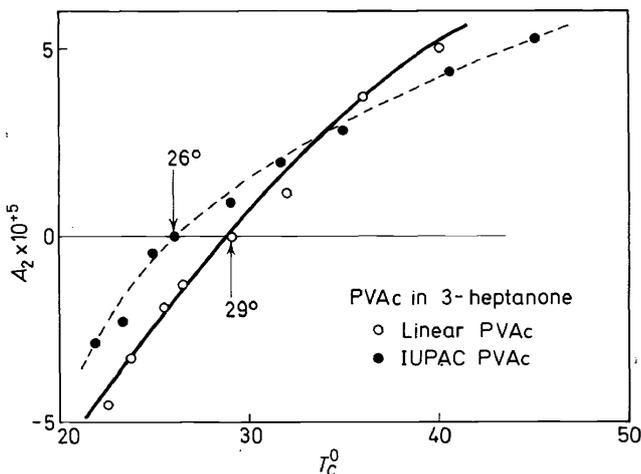


Figure 15. Determination of the  $\theta$  temperature by light scattering [ $A_2 = f(T)$ ] for a linear polyvinyl acetate (O) and IUPAC polyvinyl acetate (●).

coefficient as a function of the temperature for two samples, one linear, the other branched (PVAc—IUPAC) in 3-heptanone. This solvent is theta at 29° for the linear polymer while for the sample distributed by IUPAC and which is manifestly branched (as the viscosity measurements have shown), the second virial coefficient becomes zero at 26°C.

In conclusion, the results obtained in this work are not as good as one could have hoped, and lead to a rather pessimistic view of the precision of measurements in macromolecular physical chemistry. This is no doubt due to the fact that the problem which was posed was difficult. A more urgent problem is a detailed study of fractions. These results should lead the experimenters to make efforts to master their techniques better, taking account of certain complications resulting from high polydispersity or from branchings; it seems that in this area much more remains to be done.

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 the IUPAC. The reports which we received were often very detailed and because of lack of space we were not able to take into account all the results and all the information which was sent to us. We apologise for this to their authors.

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APPENDIX

Principal abbreviations used

PS	: polystyrene
PVAc	: polyvinyl acetate
PVC	: polyvinyl chloride
HDPE	: high density polyethylene
LDPE	: low density polyethylene
THF	: tetrahydrofuran
CCl <sub>4</sub>	: carbon tetrachloride
Ebul.	: ebulliometry
Fract.	: fractionation
VPO	: vapour pressure osmometry
Osm.	: osmometry or osmotic pressure
Visc.	: viscosity
LS	: light scattering
UC	: ultracentrifugation
GPC	: gel permeation chromatography
i.r.	: infra-red
u.v.	: ultra-violet
n.m.r.	: nuclear magnetic resonance
DTA	: differential thermal analysis
Turb.	: turbidimetry
dP	: degree of polydispersity
M <sub>n</sub>	: number average molecular weight
M <sub>w</sub>	: weight average molecular weight
M <sub>v</sub>	: viscosity average molecular weight

List of Participants in the IUPAC Programme on 'Molecular Characterization of Commercial Polymers'

The polymers studied and the techniques used by each participating laboratory are listed hereunder.

Chemische Werke Hüls (Prof. H. Hellman)  
Recklinghausen, Western Germany.

PS—PVC—HDPE—LDPE

Visc.—Osm.—LS—GPC—Fract.—x-ray—i.r.

MOLECULAR CHARACTERIZATION OF COMMERCIAL POLYMERS

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PS—HDPE—LDPE

Ebul.—Osm.—LS—i.r.

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PS—PVAc—PVC

Osm.—LS—n.m.r.

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PS—PVC—LDPE

Visc.—Osm.—LS—Fract.—Turb.

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PVC

Visc.—Osm.—GPC

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PS—PVAc

Visc.—Osm.—LS

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PS—PVAc

Visc.—Osm.—LS

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PS—PVC

Visc.—LS—UC—Fract.—i.r.

Koppers Company (Dr R. F. Kratz Jr)

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PS—HDPE—LDPE

Visc.—VPO—GPC—LS—i.r.

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Visc.—Osm.—VPO—LS—GPC

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PS—PVC

Visc.—Osm.—LS—GPC

CLAUDE STRAZIELLE AND HENRI BENOIT

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Porto Marghera, Venezia, Italy.

PVC

Visc.—Osm.—Fract.—n.m.r.—i.r.

National Bureau of Standards (Dr C. A. J. Hoeve)

Molecular Properties Section, Washington, D.C. 20234, USA.

PS—HDPE—LDPE

Visc.—LS

Allied Chemical Corporation (Dr Nakajima)

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HDPE

Visc.—Osm.—GPC—i.r.

Solvay (Dr A. Gonze)

Department of Research and Development, Brussels, Belgium.

PVC—HDPE—LDPE

Osm.—LS—UC—GPC—Fract.—i.r.—DTA—n.m.r.

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PS—PVC—LDPE

LS

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PVC

Visc.—Osm.—LS—GPC

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PS

Visc.—Osm.

B.A.S.F. (Dr Ball)

Olefin Abt. Ludwigshafen am Rhein, Western Germany.

HDPE—LDPE

GPC

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PS—HDPE—LDPE

Visc.—Osm.—Ebul.—LS—UC—GPC—i.r.

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PS

Visc.—Osm.—LS

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PS  
LS

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LS

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Visc.—Osm.—LS—GPC

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Chemical Inspectorate, Headquarters Bldg, Royal Arsenal East,  
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PS  
GPC

Unilever Forschungslaboratorium (Dr Unbehend)

Behringstrasse 154, 2 Hambourg 50, Western Germany.

PS—PVC—HDPE—LDPE  
GPC

Instituttet for Kemiindustri (Prof. J. Kops)

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PS—PVC  
Visc.—LS—GPC

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Badhuisweg 3, Amsterdam N, Holland.

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Visc.—Osm.—LS—UC—GPC—i.r.

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PS  
Osm.—LS—Fract.

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PVAc  
Viscoelasticity

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PS  
Visc.—Osm.—Fract.

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GPC

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PS  
Visc.—UC

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Osm.—LS—GPC

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PS  
Fract.—Osm.—Visc.

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LDPE—HDPE—PVC(Copernic Institute)  
Fract.—Visc.—Interferometry—Turb.

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PS  
Visc.—LS—Fract.—u.v.

Monsanto Company (Dr E. E. Drott)  
P.O. Box 1311, Texas City, Texas 77591, USA.

HDPE—LDPE  
Visc.—GPC—i.r.

Institute of Physical Chemistry (Prof. Kössler)  
7, Machova, Vinohrady, Prague 2, Czechoslovakia.

PS  
Visc.—LS—GPC—Fract.

MOLECULAR CHARACTERIZATION OF COMMERCIAL POLYMERS

Péchiney-Saint-Gobain (Dr A. de Vries)

Centre de Recherches de la Croix-de-Berny, 182/184 Av. A. Briand,  
75 Antony, France.

PS—PVC—LDPE (A)  
LS—GPC

Institut Français du Pétrole (Dr J. P. Arlie)

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PS—PVC—PVAc  
Osm.—LS—GPC

Institut Français du Caoutchouc (Dr Curchod)

42 Rue Scheffer, Paris 16, France.

PS—PVC—PVAc  
Visc.—Osm.—LS

Centre de Recherches sur les Macromolécules (Prof. H. Benoit)

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PS—PVC—PVAc  
Visc.—Osm.—LS—GPC—Fract.

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PVC—LDPE  
i.r.