

Molecular Weight Distribution by Stirring-Induced Fractional Precipitation

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SYNOPSIS

Ultrahigh molecular weight polyethylenes GUR, UTEC 2540, and UTEC 3540 were fractionated by precipitation from cooling of solutions with stirring [stirring-induced fractional precipitation (SIFP)]. The samples were dissolved in decalin and precipitated over the temperature range of 100–78°C. Three types of procedures were investigated. From fractionation data, the integral and differential molecular weight distribution (MWD) of the polymer were calculated. The MWD and average molecular weights, $\bar{M}_w$ and $\bar{M}_n$, by size exclusion chromatography (SEC) and the limiting viscosity number of the fractions and whole polymer were determined. From these data, the Mark-Houwink constants were calculated. The “ K ” and “ a ” values obtained were 6.70×10^{-4} and 0.69, respectively. The MWD curves calculated from SIFP technique by using these constants are in accordance with the MWD by SEC. Fractionation depended on the chemical nature of the stirrer and the cooling rate of the solution during precipitation. The methodology is reproducible. Faster fractionation was observed compared with other methods. © 1995 John Wiley & Sons, Inc.

Keywords: molecular weight distribution • fractional precipitation • polyethylenes • size exclusion chromatography

INTRODUCTION

Molecular weight distribution (MWD) can be obtained through fractional precipitation of polymer from solution.¹ This is an effective procedure but requires long equilibration times. Precipitation by cooling depends on a decrease in solvent power caused by a decrease in the temperature of the system. The cooling process should be sufficiently slow so that the thermodynamic equilibrium is approached. When the precipitated phase is crystalline and the polymer has much higher molecular weight (MW), in general, separation according to MW differences does not take place under these circumstances.²

Ultrahigh molecular weight polyethylene (UHMW-PE) is a crystalline polymer and its av-

erage MW is superior to one million. The crystal imperfections affect the solubility of the polymer and may interfere with the fractionation by MW. Because of the entanglement of the long chains, the diffusion of the fractions of different MWs among the coexistent phases is very slow and difficult. Thus, the fractional precipitation technique as well as the other conventional techniques,² based on the decrease in solubility of the polymer with increasing MW, were found to be unsuitable for UHMW-PE.

As the UHMW-PE properties (resistance to fatigue, wear resistance, ultimate tensile strength, etc.) are influenced by MW, both MW and MWD must be determined.

Fractionation according to MW has been observed when polymer solutions are sheared.^{3–5} A hydrodynamically induced crystallization procedure, first reported by Pennings,^{6,7} has been employed to fractionate linear polyethylene (PE),^{6–8} isotactic polypropylene (PP),⁶ and UHMW-PE.⁹ An equilibrium between a stirred polymer solution and the

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Journal of Polymer Science: Part B: Polymer Physics, Vol. 33, 759–767 (1995)
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solid polymer is established in the above procedure. Kusy and Whitley¹⁰ have reported the UHMW-PE fractionation by using an increasing temperature sequential extraction technique. It is an effective procedure but necessarily slow.

This work describes the fractionation of UHMW-PE by precipitation from decalin solutions, under far-from-equilibrium conditions. Precipitation was provoked by cooling with stirring. The method, named stirring-induced fractional precipitation (SIFP), is based on decreasing the polymer solubility when the solution is submitted to stirring or shear. Fast stirring induces the arrangement and stretching of the chains, which makes the higher MW molecules precipitate in the shape of a thin fiber onto the stirrer.^{5,7,11} The fraction thus obtained is taken off for further analysis. The next fractions are obtained at every temperature decrease of the solution with simultaneous stirring. These fractions have progressively lower MWs.

Phase separation in sheared polymer-solvent systems has been examined,¹²⁻¹⁵ and the theory of the shear-dependent phase diagrams has been worked out using the stored energy formalism.^{12,13} The basic idea is that Gibbs energy of mixing is modified by the elastic energy stored in the sheared state. Vrahopoulou and McHugh¹⁵ considered that the effect of chain stretching is equivalent to the introduction of a certain degree of rigidity to the macromolecular coils. This model led these authors to predict the formation of a flow-induced separation of liquid phase concurrent with MW fractionation.

In this work, viscosity average molecular weight ($\bar{M}_v$) and MWD by size exclusion chromatography (SEC) for the fractions and the whole polymer were determined. The integral and differential MWD as well as the Mark-Houwink constants in *cis*, *trans*-decahydronaphthalene (decalin) were calculated from fractionation data.

EXPERIMENTAL

Materials

The samples of UHMW-PE used were type Hostalen GUR ($[\eta] = 14.22$ dL/g in decalin at 135°C) from Höchst-German, and UTEC 2540 ($[\eta] = 15.62$ dL/g) and UTEC 3540 ($[\eta] = 16.98$ dL/g) from Polialden. In the fractionation experiments, UHMW-PE was dissolved in decalin from Riedel-de-Häen at 150°C and at a concentration of 0.1 g/dL of solvent, except where otherwise indicated. All solutions were stabilized with 0.1 wt % of the antioxidant Ir-

ganox 1010. The polymers and the solutions were kept at all times under purified nitrogen, to prevent oxidative degradation.

Fractionation

Fractionation was done by decreasing the temperature of 300 mL of a solution from 150 to 78–80°C, under stirring. The apparatus used was a four-necked glass container ($\phi = 9$ cm, 14 cm height) disposed on a magnetic stirrer and equipped with a digital thermometer, a reflux condenser, an N_2 stream, and a mechanical stirrer. An ordinary stainless steel stirrer equipped with two paddles in triangle shape (1.5 cm $\times$ 3.0 cm $\times$ 3.0 cm) was used, except where otherwise indicated. The container and the N_2 stream were thermostatted using a silicone oil bath that the temperature was controlled within $\pm 0.1^\circ\text{C}$.

Three types of procedures were followed. According to procedure A, Experiments A1, A2, A3, and A4 were carried out for which the cooling of the solutions was as follows:

- i) from 150 to 130°C at 0.8°C/min with occasional and gentle magnetic stirring,
- ii) from 130°C to a preestablished precipitation temperature, T_p , of 100°C at 0.5°C/min under mechanical stirring at a speed of 400 rpm,
- iii) the precipitation temperature, T_p , was kept constant for a preestablished period (precipitation time, t_p); afterwards the stirring was stopped and the precipitate formed on the stirrer (fraction) was removed,
- iv) stirring and cooling (cooling rate equal to 0.08, 0.14, 0.10, and 0.19°C/min, Table I) were picked up. The solution was cooled until another T_p was reached, then step iii was repeated. Steps iii and iv were consecutively repeated, so the subsequent fractions were obtained at every temperature decrease.

The precipitation times (t_p) and the precipitation temperatures (T_p) are shown in Table II.

Procedure B was also done in four steps, but the cooling of the solution in steps i, ii, and iv was: i) from 150 to 106°C at 0.7°C/min; ii) from 106 to 99°C at 0.2°C/min; iv) at an average rate of 0.05 or 0.10°C/min, using a stainless steel stirrer or a Teflon stirrer (Table I). The fractions were obtained at every 1 or 2°C of temperature decrease (Table II). The more important differences between procedures A and B are in step ii. They are the temperature and

Table I. Summary of the Experiments

Experiments	A1	A2	B1	B2	B3	C	A3	A4
Samples	GUR	GUR	GUR	GUR	GUR	GUR	UTEC2540	UTEC3540
Sol. conc. (g/dL)	0.10	0.10	0.10	0.10	0.10	0.20	0.10	0.10
Cooling rate in step iv (°C/min)	0.08	0.14	0.10	0.05	0.10	0.08	0.10	0.19
Type of stirrer	ss	ss	ss	ss	Teflon	ss	ss	ss

ss: stainless steel.

the time period in which the solutions are submitted to mechanical stirrer before precipitation.

Procedure C was the same procedure A but was done in two periods. In the first one, the solution was cooled from 150 to 95.8°C; 37% of the polymer was separated in three fractions. The remaining polymer was then precipitated by fast cooling without stirring. In the second period, the precipitated polymer was redissolved at 150°C, cooled to 94.4°C, and further fractionated to obtain 13 fractions. The experimental conditions are described in Tables I and II.

Sixteen to 20 fractions removed were washed with CCl₄ (reagent grade) and were dried to constant

weight at 60°C and 400 mmHg pressure, under N₂ atmosphere. Limiting viscosity number [η], viscosity average molecular weight ($\bar{M}_v$), and infrared spectra and MWD by SEC and from fractionation data were determined.

Viscosity Average Molecular Weight ($\bar{M}_v$)

The viscosities were measured in a Ubbelohde viscometer at 135°C using decalin as solvent. At least three flow times were obtained to ± 0.2 s. To prevent incomplete dissolution and degradation, the solutions were prepared by the heating of fractions and solvent, in a closed bottle nitrogen saturated, up to

Table II. Time and Temperature of Precipitation for the UHMW-PE Fractionation by SIFP

Frac. No.	t_p (min)	Precipitation Temperature, T_p (°C)							
		Exp. A1	Exp. A2	Exp. B1	Exp. B2	Exp. B3	Exp. C	Exp. A3	Exp. A4 ^a
1	60	100.1	100.4	99	99	99	100.2	101.2	101.1
2	60	99.6	99.4	98	98	98	98.7	100.6	99.5
3	60	98.3	97.8	97	97	97	95.8	98.6	99.2
4	30	97.2	96.6	96	96	96	94.4	98.0	99.1
5	30	94.0	94.8	95	95	95	94.0	94.9	98.9
6	5	92.2	93.9	94	94	94	92.6	93.3	98.3
7	5	91.2	93.4	93	93	93	91.7	94.0	98.0
8	5	90.0	91.6	92	92	92	90.9	91.6	97.8
9	5	88.7	90.3	91	91	91	88.7	90.1	93.1
10	5	86.6	89.7	90	90	90	87.9	89.1	96.7
11	5	85.2	88.5	89	89	89	86.8	88.0	95.2
12	5	84.2	86.6	87	88	88	85.0	85.9	92.0
13	5	83.2	85.5	85	86	86	83.2	83.9	90.9
14	5	81.8	84.0	83	84	85	82.9	81.1	89.0
15	5	80.3	82.5	81	82	84	80.4	77.8	87.5
16	5	78.5	80.0	^b	80	82	78.5	77.4	85.7
17	5		78.8			80		^b	84.0
18	5					78			82.3
19	5								81.5
20	5								80.3

^a Fast precipitation was observed and caused difficulty in the temperature control.^b A residue was collected by precipitation with methanol.

180°C for 1 h with occasional and gentle stirring. An antioxidant (2,6-di-*tert*-butyl-4-methyl-phenol, BHT) at a concentration of 0.2 wt % was employed. The antioxidant at this concentration had no effect on the limiting viscosity number ($[\eta]$) (ref. 10), which was evaluated from the Schulz-Blaschke relationship¹⁶

$$\eta_{sp}/c = [\eta](1 + 0.29\eta_{sp}) \quad (1)$$

where η_{sp} is the specific viscosity and c is the concentration (g/dL). $\bar{M}_v$ was calculated from the Mark-Houwink equation (" K " = 6.76×10^{-4} ; " a_η " = 0.67).^{17,18}

Size Exclusion Chromatography (SEC)

Samples of the GUR as well as some fractions were run separately in a Waters 150C SEC apparatus in 1, 2, 4, trichlorobenzene (HPLC degree), at 140°C, containing 0.05 wt % of BHT purified. The solution concentration was 0.1 mg/mL of solvent. Analyses were made by using four columns of the Phenomenex type (pore size = 10^6 , 10^5 , 10^4 , 10^3 Å). For the UHMW-PE fractionation it is more appropriate to use four columns with 10^7 , 10^6 , and 10^5 Å pore size. Therefore, a portion of the sample in the range of the highest MW may not be adequately fractionated, leading to average molecular weight ($\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$) values smaller than the real values. The SEC system was calibrated by using PS standards (peak molecular weight, $M_p = 3 \times 10^5$ to 2×10^7). Standards with M_p between 1×10^7 and 2×10^7 suffer degradation during the measurements and were therefore left out.

Molecular Weight Distribution From Fractionation Data

The Schulz's¹⁹ technique was used to calculate the integral distribution curve. The cumulative weight fraction, $C(M_i)$, for the i th fraction was computed by adding one-half of its weight fraction (W_i) to the weight fraction of all previous fractions:

$$C(M_i) = W_i/2 + \sum_{j=1}^{i-1} W_j \quad (2)$$

The cumulative distribution, $C(M_i)$ vs. molecular weight of the fractions (M_i), was then obtained.

The differential distribution function $M.f(M)$ was evaluated by the Goodrich method²⁰ by using the equations

$$M.f(M) \cong a(aM)^s \exp(-aM) \sum_{n=0}^4 c_n P^n(aM) \quad (3)$$

$$s = \frac{2 - \mu_3\mu_1\mu_2^{-2}}{\mu_3\mu_1\mu_2^{-2} - 1} \quad (4)$$

$$a = (s + 1)\mu_1\mu_2^{-1} \quad (5)$$

$$c_n = \sum_{r=0}^n h_{n,r} a^r \mu_{r+1} \quad (n, r = 0, 1, 2, 3, 4). \quad (6)$$

Both a and s are pre-fixed. Using these values, the moments of the distribution (μ) can be evaluated from tables²⁰ and from the integral distribution curve. From these μ values, new values for a and s are then calculated from eqs. (4) and (5). By an iterative procedure, the μ available values can be reached. The matrice elements ($h_{n,r}$) in eq. (6) and the Laguerre polynomials [$P^n(aM)$] in eq. (3) are determined from tables,²⁰ too. The average molecular weights are $\bar{M}_n = \mu_1\mu_0^{-1}$; $\bar{M}_w = \mu_2\mu_1^{-1}$; $\bar{M}_z = \mu_3\mu_2^{-1}$. Average molecular weights were also computed by fitting the data to a log-normal distribution function.¹⁹ The M_0 and β values of this function were determined by plotting the fractionation data $C(M_i)$ against $\log(M_i)$ on a logarithmic sum probability grid. The average molecular weights are: $\bar{M}_n = M_0 \exp(-\beta^2/4)$; $\bar{M}_w = M_0 \exp(\beta^2/4)$; $\bar{M}_z = M_0 \exp(3\beta^2/4)$. The consistency of the fractionation data was investigated from Phillippoff rule^{16,21} by using eq. (7):

$$E = [\eta]_w/[\eta]_s \quad (7)$$

where $[\eta]_w = \sum (W_i[\eta]_i)/\sum W_i$; $[\eta]_s$ and $[\eta]_i$ are the limiting viscosity numbers of the whole sample and of the fraction i , respectively.

Infrared Spectroscopy

For the detection of possible thermo-oxidative degradation of the polymer chains, infrared spectra were taken of some fractions. The samples were press-molded between two aluminium sheets at 50 Kg/cm² of pressure and 190°C for 3 min. Spectra were recorded immediately thereafter and also after extraction in chloroform for 2 h at 70°C. A Soxhlet extraction apparatus was used. Spectra were obtained with a Nicolet 710 FTIR spectrometer at a resolution of 2 cm⁻¹, and 100 scans were signal-averaged for each sample.

Table III. Fractionation Data for UHMW-PE (GUR)

$[\eta]$ (dL/g)	$\bar{M}_v^a \times 10^{-6}$	Weight Frac. W Exp. A1	Weight Frac. W Exp. A2	$[\eta]$ (dL/g)	$\bar{M}_v^a \times 10^{-6}$	Weight Frac. W Exp. B1	Weight Frac. W Exp. B2
^b		0.0142	0.0162	^b		0.0073	0.0130
^b			0.0080	^b		0.0073	0.0153
13.62	2.66	0.0080		16.96	3.69		0.0570
		0.0327	0.0149			0.0334	0.0732
16.57	3.55		0.0458	16.25	3.46		0.0901
16.23	3.45	0.0473		15.99	3.37	0.0526	
14.47	2.91	0.2982				0.1481	
13.48	2.61		0.1978	15.96	3.37		0.0523
		0.0731	0.0698	13.98	2.76		0.1027
13.02	2.48		0.0273	13.96	2.76	0.0403	
			0.0502			0.0176	
12.52	2.34		0.0400	12.55	2.35		0.0157
11.86	2.16	0.0218		12.49	2.33	0.0967	
		0.0182	0.0284			0.0579	0.0287
10.46	1.79		0.0265	12.28	2.28		0.0417
9.30	1.50		0.0411	11.21	1.99	0.0169	
9.06	1.45	0.0167				0.0253	0.0673
		0.0411	0.0665	10.76	1.87		0.0177
8.08	1.22	0.0284		9.63	1.58		0.0590
7.80	1.15		0.0560	8.73	1.37		0.0527
			0.0396	8.31	1.27	0.0161	
			0.0669			0.1343	0.1341
6.92	0.96	0.1055		8.18	1.24		0.1794
7.25	1.03		0.1400	7.03	0.99	0.1078	
7.35	1.06	0.1284		7.19	1.02	0.1607	
		0.0600				0.0779	
$\Sigma =$		1.0000	1.0000			1.0000	1.0000

^a $K = 6.76 \times 10^{-4}$, $a_\eta = 0.67$.

^b This fraction did not redissolve in decalin; its viscosity couldn't be determined.

RESULTS AND DISCUSSION

Fractionation of UHMW-PE GUR

Fractionation data of Experiments A1, A2, B1, and B2 are summarized in Table III. The integral, $C(M_i)$, and differential, $M_f(M)$, distribution curves depicted in Figure 1b and Figure 2 were calculated from these data. It can be seen that some experimental points do not lie perfectly on the smooth curve on the integral distribution plot. Such scattering is mainly due to nonuniformity of the fraction size. It also depends on the MWD of the fractions and the accuracy involved in the determination of $\bar{M}_v$.¹⁹ If a large fraction is obtained next to a small one, the accuracy in the determination of the cumulative weight fractions [eq. (2)] is affected and the experimental points will appear scattered.¹⁹

In Figure 1, the MWD curves determined by SIFP are compared with the MWD curve by SEC. Curves similar to these were found in the literature¹⁰ for

UHMW-PE. The shape of the curves apparently is the same but the MWD by SEC indicates molecular weights smaller than by SIFP. This behavior is re-

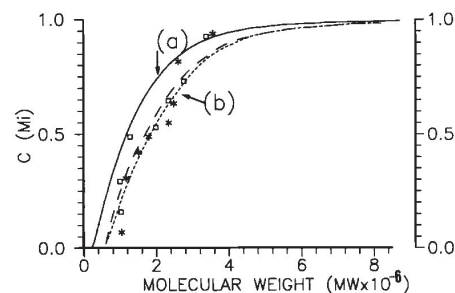


Figure 1. Integral molecular weight distribution of UHMW-PE (GUR): (a) by SEC (—), (b) by stirring-induced fractional precipitation, Exp. A1 (----) and Exps. A2 and B1 (···). The data points of Exp. A2 (*) and Exp. B1 (□) were calculated using $K = 6.76 \times 10^{-4}$ and $a_\eta = 0.67$.

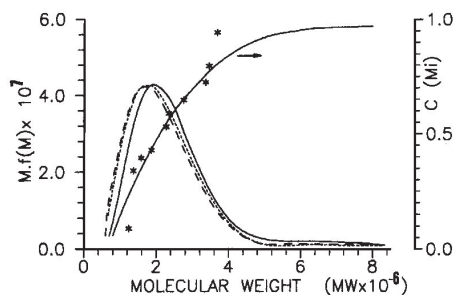


Figure 2. Differential, $M.f(M)$, and integral, $C(M_i)$, molecular weight distribution of UHMW-PE (GUR): Exp. A1 (---); Exps. A2 and B1 (···); Exp. B2 (—) (* — *).

lated to the use of the Mark-Houwink equation for the calculation of MW of the fractions and will be discussed in more detail in the next section.

The differential distribution curves are compared in Figure 2. The curves of Exps. A2 and B1 are coincident. The curve of Exp. A1 is concordant with that obtained in Exps. A2 and B1; the corresponding molecular weights do not differ among themselves more than 0.6%. The curve of Exp. B2 indicates higher molecular weights than in the former experiments. The average MWs calculated from these curves are shown in Table IV. As expected, $\bar{M}_w$ in Exp. B2 (2.50×10^6) is higher than in Exps. B1, A2, and A1 and is more close to $\bar{M}_v$ of the unfractionated polymer ($\bar{M}_w \cong \bar{M}_v = 2.83 \times 10^6$). The ratio between $[\eta]_w$ obtained from fractionation data and $[\eta]_i$ of initial polymer, from eq. (7), was higher for Exp. B2 ($E = 0.92$) than for Exps. B1, A2, and A1 ($E = 0.88$, 0.87, and 0.85, respectively). These results together show that better fractionation was obtained in Exp. B2.

Because a log-normal MWD has been observed in the literature for UHMW-PE,^{9,10} the average MW in Exp. B2 was also calculated using the log-normal function (Table IV). The $\bar{M}_w$ obtained (2.68×10^6) is more accordant with the $\bar{M}_v$ of the unfractionated

polymer ($\bar{M}_w \cong \bar{M}_v = 2.83 \times 10^6$) than the $\bar{M}_w$ obtained from the Goodrich method (2.50×10^6). However, we observed that the log-normal function did not fit well to the points in the range of smaller MWs. This finding is in accordance with Wagner and Dillon' results.⁹

The fact that the values of $\bar{M}_w$ calculated from distribution curves are smaller than $\bar{M}_v$ of the unfractionated polymer can be due to: i) gentle degradation of some fractions during the measurements of viscosity or ii) difficulties in the precise determination of $\bar{M}_v$ of the fractions of highest MW because they were resistant to redissolving or because $[\eta]$ and consequently $\bar{M}_v$ depend greatly on the shear rate in a capillary viscometer.^{9,10} Degradation during the fractionation was investigated by FTIR. Spectra of some fractions were taken before and after extraction with chloroform. Before extraction, absorptions at 1740 cm^{-1} were observed, characteristic of ester carbonyl. After extraction, these absorptions disappeared. The compound extracted was identified as Irganox 1010. So we conclude that there was not any thermo-oxidative degradation in these fractions during the fractionation period. The error involved in the determination of $\bar{M}_v$ of the fractions appears to be the main cause of the differences observed among $\bar{M}_w$ from fractionation data and $\bar{M}_v$ of unfractionated polymer.

The effect of the stirrer type on the fractionation was investigated from Exps. B3 (Teflon stirrer), A2, and B1 (stainless steel stirrer) and can be seen comparing Figure 3 with Figure 1. In Figure 3, the experimental points of Exp. B3, in the range of 3.0×10^6 to 3.8×10^6 , are close to the MDW curve obtained in Exps. A2 and B1. The experimental points of Exps. A2 and B1 (Fig. 1) are farther from the MWD curve than in the case of Exp. B3. This was attributed to greater mass and uniformity of size (not shown) of the fractions in Exp. B3 than in Exps. A2 and B1. In Exp. B3, the mass of the fractions 1, 2, 3, and 4 was one to five times greater than in Exps. A2 and B1 (Table III). For MWs smaller than 3.0×10^6 , the mass of the fractions in Exp. B3 was

Table IV. Average Molecular Weights for UHMW-PE (GUR) by SIFP

	Exp. A1 ^a	Exps. A2, B1 ^a	Exp. B2 ^a	Exp. B2 ^b
$\bar{M}_w \times 10^{-6}$	2.32	2.38	2.50	2.68
$\bar{M}_w/\bar{M}_n$	1.4	1.4	1.4	1.7
$\bar{M}_z \times 10^{-6}$	3.65	3.39	3.40	4.61

^a Values calculated using the Goodrich method.

^b Values calculated from a log-normal function.

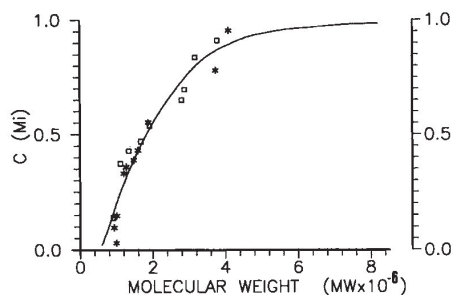


Figure 3. Comparison between the data points obtained in Exp. B3 ($\square$) and Exp. C ($*$) with the integral MWD curve of Exps. A2 and B1 (—). Exp. B3 was carried out using a Teflon stirrer; Exps. A2 and B1 using a stainless steel stirrer; Exp. C was carried out in two periods, using a stainless steel stirrer.

sometimes too big, sometimes too small; consequently the points show greater deviations of the curve. Therefore, the mass of the fractions formed on the stirrer depends on the chemical nature of the stirrer (Teflon or stainless steel). A similar behavior pattern has been found in the literature. As indicated,^{22,23} the amount of PE fibers formed from solutions, by a hydrodynamically induced crystallization procedure, was greater on a Teflon surface than on a steel surface. It also depended on stirrer shape.²⁴

The above results lead us to conclude that better fractionation is achieved in the range of higher MW by using the Teflon stirrer (Exp. B3) than with the stainless steel stirrer (Exps. A2 and B1). For MWs smaller than 3.0×10^6 , the reverse holds true.

The results of Exp. C are shown in Figure 3. As indicated earlier, Exp. C was carried out in two periods. Precipitation temperatures covered an interval from 100.2 to 95.8°C in the first one, obtaining three fractions, and covered an interval from 94.4 to 78.5°C in the second one, separating 13 fractions. The experimental points that correspond to the fractions obtained in the second period ($MW < 2.2$

$\times 10^6$) are approximately on the same curve of Exps. A2 and B1. We conclude, thus, that the experimental MWD curve depends on whether the precipitation is carried out in a single period (Exps. A2 and B1) or whether a double precipitation in two periods (Exp. C) is made.

From all results presented we conclude that i) the MWD curves obtained depended on procedures followed in Exps. A2, B1, and C; ii) the fractionation depended on the chemical nature of the stirrer; better fractionation was obtained in the range of higher MW using a Teflon stirrer (Exp. B3) than a stainless steel stirrer (Exps. A2 and B1); iii) following procedure B, better fractionation was observed when the cooling rate in step iv was $0.05^\circ\text{C}/\text{min}$ (Exp. B2). We conclude that SIFP is a reproducible and reliable methodology.

The Mark-Houwink constants

From an investigation of all the Mark-Houwink constants reported in the literature for UHMW-PE, one found the following values: 6.2×10^{-4} , 0.70 (ref. 25); 3.5×10^{-4} , 0.73 (ref. 26); 3.1×10^{-4} , 0.74 (ref. 10); 6.7×10^{-4} , 0.67 (ref. 27); 4.6×10^{-4} , 0.73 (ref. 27); 4.32×10^{-4} , 0.72 (ref. 10). Using these constants, the $\bar{M}_v$ for an UHMW-PE with $[\eta] = 14.22 \text{ dL/g}$ may be 1.4×10^6 , 1.7×10^6 , 1.9×10^6 , 2.0×10^6 , or 2.9×10^6 . Because of this variety of values, we determine the Mark-Houwink constants.

The $[\eta]$, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ for some fractions and whole polymer were determined independently by SEC and by viscometer (Table V). These data made possible the establishment of a Mark-Houwink relationship for the MW range between 0.72×10^6 and 2.4×10^6 at 135°C . The K and a_η values were determined from the curve of $\log [\eta]$ against $\log \bar{M}_w$. The $\bar{M}_v$ was then determined from the following approximation, which holds for distributions that are not too wide ($\bar{M}_w/\bar{M}_n < 2$):²⁸

$$\bar{M}_v/\bar{M}_n = (1 - a_\eta)/2 + (1 + a_\eta)\bar{M}_w/2\bar{M}_n \quad (8)$$

Table V. Limiting Viscosity Number and MW by SEC for UHMW-PE (GUR) and Some Fractions of Exp. A1

Fraction No.	Temperature T_p ($^\circ\text{C}$)	$[\eta]$ (dL/g)	$\bar{M}_w \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$
4	97.2	16.23	2.383	1.9
5	94.0	14.47	2.137	1.9
8	90.0	11.56	1.505	1.8
14	81.8	6.92	0.719	2.3
GUR		14.22	1.719	1.9

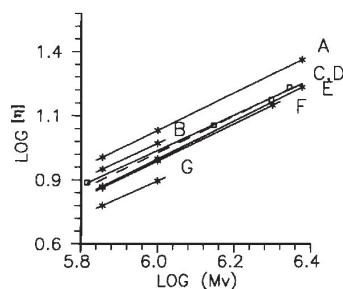


Figure 4. Mark-Houwink relationship for PE in decalin at 135°C. K and a_η equal to: (A) 4.6×10^{-4} , 0.73 (ref. 27); (B) 6.2×10^{-4} , 0.70 (ref. 25); (C) 6.70×10^{-4} , 0.69 ($\square$ — $\square$), values obtained in this work; (D) 4.32×10^{-4} , 0.72 (the dashed line represents the regression line of the end points of all relationship) (ref. 10); (E) 3.1×10^{-4} , 0.74 (ref. 10); (F) 3.5×10^{-4} , 0.73 (ref. 26); (G) 6.70×10^{-4} , 0.67 (ref. 27).

Finally, $\log[\eta]$ is plotted against $\log \bar{M}_v$; K , and a_η were again evaluated. This procedure was continued as long as K and a_η ceased to change on further iteration. The values obtained were 6.70×10^{-4} and 0.69, respectively, with a correlation coefficient of 100%. Our result is compared with the results reported in the literature in Figure 4. It is close to the curve that represent the average value of all the equations obtained from a linear regression analysis of the endpoints of all lines by Kusy and Whitley.¹⁰

In Table V, the $\bar{M}_w/\bar{M}_n$ ratio for the fractions 4, 5, 8, and whole polymer are equivalents among themselves. This is not usual and can be due to incomplete fractionation by SEC, in the range of higher MWs, due to pore size of the columns used.

As it was seen earlier, the MDW curve obtained

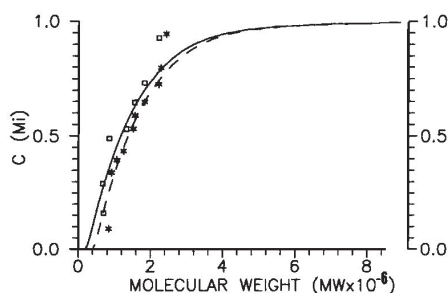


Figure 5. Comparison between the integral MWD curves of UHMW-PE (GUR) obtained by stirring-induced fractional precipitation, Exp. B1 ($\square$) and Exp. B2 (*---*), with that obtained by SEC (—). The experimental points ($\square$) and (*) were calculated using the new constants, $K = 6.70 \times 10^{-4}$ and $a_\eta = 0.69$.

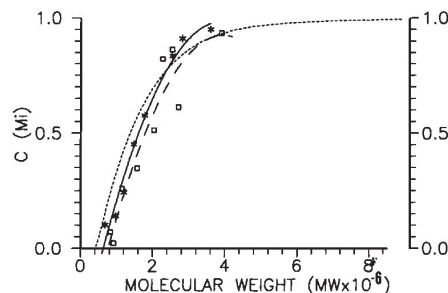


Figure 6. Integral molecular weight distribution by stirring-induced fractional precipitation for UHMW-PE: GUR (· · ·), UTEC 2540 (*—*), and UTEC 3540 ($\square$ --- $\square$). The corresponding experiments were Exps. B2, A3, and A4, respectively.

by SEC indicated MWs smaller than by SIFP (Fig. 1). For this reason, the $\bar{M}_v$ of the whole polymer and the integral MWD curves for Exps. B1 and B2 were recalculated using the new constants determined (Fig. 5). The experimental points obtained in Exp. B1 are consistent with the SEC curve. The curve obtained in Exp. B2 indicates MW values larger than that found by SEC. In Exp. B1, $\bar{M}_w = 1.72 \times 10^6$ is 8.0% smaller than $\bar{M}_v$ of the whole polymer (1.87×10^6) by viscometer. In Exp. B2, $\bar{M}_w = 1.82 \times 10^6$ is close to $\bar{M}_v$ of the whole polymer. This was expected since fractionation in Exp. B2 was better than in Exp. B1.

Fractionation of UHMW-PE UTEC 2540 and 3540

The integral MWD calculated by using the new constants ($K = 6.70 \times 10^{-4}$ and $a_\eta = 0.69$) can be seen in Figure 6. The $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ were determined by adjusting the points to a log-normal distribution function.¹⁹ The values obtained were 1.82×10^6 , 1.3 for UTEC 2540 and 2.48×10^6 , 1.5 for UTEC 3540, respectively. The function parameters were $M_0 = 1.62 \times 10^6$, $\beta = 0.684$ for UTEC 2540 and $M_0 = 2.04 \times 10^6$, $\beta = 0.879$ for UTEC 3540. UTEC 3540 ($\bar{M}_v = 2.41 \times 10^6$) has a rather larger MWD than UTEC 2540 ($\bar{M}_v = 2.14 \times 10^6$).

CONCLUSION

According to the experiments carried out, it was concluded that:

1. UHMW-PE can be fractionated and its MWD can be evaluated by using the stirring-induced fractional precipitation technique.

2. Faster fractionation was observed compared to other methods.^{7,10} Fractionation required 17 h and amounts as small as 0.3 g of samples can be analyzed.
3. The plot of $\log[\eta]$ vs. $\log \bar{M}_v$ of some fractions indicated that the Mark-Houwink constants in decalin at 135°C are 6.70×10^{-4} and 0.69 for the MW range from 0.72×10^6 to 2.4×10^6 .
4. The fractionation data indicated that:
 - (a) UHMW-PE GUR has species that $[\eta]$ ranges from 6 to 24 dL/g,
 - (b) approximately 50% of the UHMW-PE GUR has $[\eta]$ between 8.0 to 14.8 dL/g,
 - (c) less than 8% of the material has $[\eta] > 20.8$ dL/g,
 - (d) better fractionation occurred in the region of medium to small MW.
5. With the proposed methodology it is possible to distinguish UHMW-PE from different grades.

We are thankful to Polialden Petroquímica S.A. for provision of samples and equipment.

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Received February 18, 1994

Revised October 3, 1994

Accepted October 11, 1994