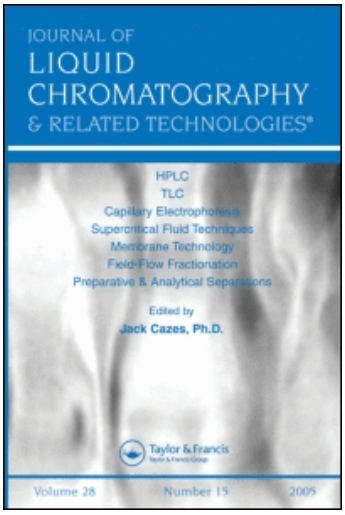

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High Temperature GPC with a Single Capillary Viscometer

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HIGH TEMPERATURE GPC WITH A SINGLE CAPILLARY VISCOMETER*

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INTRODUCTION

The purpose of this paper is to discuss the results obtained with high temperature GPC using a WATERS GPC 150CV equipped with a single capillary viscometer (SCV) and a differential refractive index detector (DRI) prototype. The reason for using a DRI prototype is that it has been demonstrated that a standard DRI detector may lead, under certain conditions, to erroneous results in viscosity calculations because of the occurrence of a very small flow fluctuation so-called "Lesec effect" when the polymer flows across the detectors (1-3). This very small fluctuation is enough to produce a significant apparent shift of the viscometer peak and leads to a small rotation of the viscosity law. The consequence is an abnormal small decrease of the Mark-Houwink **a** exponent. This phenomenon is caused by the specific viscosity of the polymer solution increasing the pressure drop in the detector area (1-3).

Furthermore, GPC-Viscometry requires a calibration curve in molecular weight, usually a "universal calibration curve" $Log([\eta]*M)=f(Ve)$ (4). As for classical GPC, perfect control of solvent flow rate is required, since molecular weights of broad polymers are calculated by comparison of their sliced distribution with elution volumes of narrow standards. The use of the SCV allows

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perfect control of the flow rate and this small flow fluctuation is not sufficient to introduce a significant error in molecular weight calculations when referring to a calibration curve. It only leads to a very small viscometer peak distortion and a decrease of the viscosity law **a** exponent.

The purpose of this study is to check the behavior of a DRI prototype at high temperature. This prototype has been designed to avoid the occurrence of the flow fluctuation that may occur with a standard DRI.

INSTRUMENTATION AND GENERAL CONSIDERATIONS.

The single capillary viscometer.

The Single Capillary Viscometer (SCV) is used inside the WATERS GPC 150CV instrument (5). It is composed of a capillary tube with the following characteristics (length=6", internal diameter=0.014", volume=18 µl) and of a differential pressure transducer (5 KPA full scale) connected to both capillary ends to measure the pressure drop across the capillary.

SCV obeys Poiseuille's law and the pressure drop P across the capillary depends upon the capillary geometry (radius r and length l), on the flow rate Q and on the viscosity η according to:

$$P = 8 / \pi * l / r^4 * \eta * Q$$

At constant flow rate Q, the pressure drop is proportional to viscosity η and, at constant viscosity η, the pressure drop is proportional to flow rate Q. Consequently, in order to use the SCV as an accurate viscometer, the flow rate must be maintained absolutely constant during the GPC experiment. Conversely, SCV allows perfect control of flow rate and is also used as a very powerful troubleshooting tool.

The flow fluctuation ("Lesec effect").

It has been shown that the standard DRI detector, but also every instrument using long capillary connecting tubes in the detector area, may lead to an abnormal behavior of the viscometric detection (1-3) but also possibly with other detectors. A flow fluctuation occurs when the polymer solution, with a higher specific viscosity than solvent, flows through the detectors, increasing the pressure drop. This weak flow fluctuation slightly distorts the viscometer peak and produces an apparent peak shift downstream. This apparent shift introduces a mismatch between the slice concentration information from the DRI and the slice pressure information from the viscometer. This mismatch leads to a slightly

incorrect calculation of the slice intrinsic viscosity $[\eta]_i$. As this effect is very weak, the errors on intrinsic viscosity are almost negligible but they lead to a slight rotation of the Mark-Houwink plot and a slight decrease of the Mark-Houwink **a** exponent.

Unfortunately, with GPC-Viscometry, the exponent **a** value has a physical meaning (**a**=0.5 for poor solvents, **a**=0.8 for good solvents, higher value for rigid polymers) and it must be determined very accurately. Also, for branched polymers, the branching distribution g'_i being calculated by dividing the experimental intrinsic viscosity $[\eta]_{br_i}$ by the $[\eta]_{lin_i}$ value of the corresponding linear polymer at the same molecular weight, the calculation of the branching distribution would be also affected by this effect. For these reasons, as the flow fluctuation cannot be readily corrected, it must be eliminated by an appropriate modification of the hardware.

The differential refractive index detector prototype.

For this study, a DRI prototype has been built with a geometry designed to avoid the flow fluctuation. The 0.009" inlet tubing has been replaced by a 0.020" tubing. The ratio in diameter being 2.22, we can expect, according to Poiseuille, a decrease of the pressure drop by a factor of 24 for the same length, but at the same time, we get an increase of internal volume by a factor of 5 that is unacceptable. For this reason, the internal design has been modified to reduce this volume. This detector, called prototype #1, having an internal volume around 150 µl, was first successfully tested at room temperature with THF (2). Nevertheless, the results obtained with this prototype show a small discrepancy of 25 µl between the interdetector volume value and the value necessary to run broad sample perfectly, probably due to excessive internal volume (interdetector volume being 150 µl plus the half of detector cells 13 µl, i.e. around 165 µl).

In order to improve the detector performance, the internal geometry of prototype #1 has been modified to give prototype #2. The inlet tubing having an internal volume of around 87 µl, interdetector volume is 87µl plus the half of detector cells 13 µl, i.e. around 100 µl. This is the DRI prototype that has been used in this high temperature study.

EXPERIMENTAL RESULTS.

Experimental conditions.

A WATERS GPC 150CV, equipped with the DRI prototype #2 described above, was used for this study. The solvent was 1,2,4-trichlorobenzene (TCB) at a temperature of 145°C and a flow rate of 1 ml/mn. TCB was filtered through

basic alumina to remove acidity and through Millipore membrane type FH 0.45μ. Then, a stabilizer (Irganox 1010) was added at a concentration of 0.1 %. The sample solutions were prepared at a concentration of approximately 0.001 g/ml at 170°C for 1 hour without stirring to avoid mechanical degradation, then at 150°C during 2 hours with stirring. They were overprotected at a concentration of 0.2 % of Irganox 1010 to avoid chemical degradation.

The columns used were a set of WATERS Ultrastyragel (10^3, 10^4, 10^5 and 10^6 Å). The narrow standards used were a set of polymethylmethacrylate (PMMA) from POLYMER LABORATORIES and a set of polystyrene (PS-TSK) from TOYO SODA.

The GPC software.

The software is the "Multidetector GPC software", a PC-DOS package written by J. Lesec (6) for triple detection GPC. For data acquisition, the PC computer is connected to the 150 CV through a CEC IEEE board (CAPITAL EQUIPMENT CORPORATION) and a 199 scanner/multimeter (KEITHLEY). Molecular weights are calculated either using a universal calibration curve or a combination of the classical molecular weight calibration curve and the viscosity law of the standards.

The data area is determined by the extreme bounds of both peaks to run calculations on the totality of peak information, a special procedure of extrapolation being used to recover missing data at both ends of chromatograms (6). The same holds true for intrinsic viscosity $[\eta]_i$ versus elution volume and versus Log(M), the central part of data being used to extrapolate and to re-build noisy data out of bounds at both ends of $[\eta]_i$ data. In addition to the average molecular weights, intrinsic viscosity $[\eta]$, Mark-Houwink K and **a** coefficients, DRI area constant and refractive index increment dn/dc are calculated. For branched polymers, the branching distribution g'_i is calculated by dividing the experimental intrinsic viscosity $[\eta]_{br_i}$ by the $[\eta]_{lin_i}$ value of the corresponding linear polymer at the same molecular weight. Average g' <g'>, g'_i at Mn, g'_i at Mw, g'_i at Mz and molecular weight where branching begins to occur are also calculated.

Another available advantage is the ability to calculate the number average molecular weight Mn from the viscometer without using the concentration detector data. A calculation method was originally described by J.M. Goldwasser (7). The GPC software uses a different method similar to the one described later by W. Yau (8). As Mn is defined as:

$$Mn = \Sigma C_i / \Sigma (C_i / M_i)$$

when multiplying (C_i / M_i) by $[\eta]_i$ at numerator and denominator, it comes:

$$(C_i / M_i) = (C_i*[\eta]_i / M_i*[\eta]_i)$$

and $$Mn = \Sigma C_i / \Sigma (C_i*[\eta]_i / M_i*[\eta]_i)$$

ΣC_i is the sample concentration Conc (using the injection concentration C_i, the injection volume and the slice volume). $M_i*[\eta]_i$ is the hydrodynamic volume HV_i coming from universal calibration. $C_i*[\eta]_i$ is the viscometer response when using the following formula to calculate $[\eta]_i$ at zero concentration:

$$[\eta]_i = [\ 2/C_i * (\eta_{redi} - \eta_{inhi})\ ]^{0.5}$$

using: $\eta_{redi} = 1/C_i * ((P_i - P_0) / P_0)$ and $\eta_{inhi} = 1/C_i * Log\ (P_i / P_0)$

it comes that the viscometer value $Visco_i = C_i*[\eta]_i$ with:

$$C_i*[\eta]_i = [\ 2 * (\ (P_i-P_0)/P_0 - Log\ (P_i/P_0)\ ]^{0.5}$$

Finally:

$$Mn = Conc / \Sigma (\ Visco_i / HV_i)$$

Using this formula, it is possible to calculate Mn by an absolute procedure using only the sample concentration Conc, the viscometer signal $Visco_i$ and a universal calibration curve HV_i without the need of any constant or any assumption and without need of the concentration detector. This feature is particularly useful to check the validity of results and when studying copolymers with a variable composition for which the DRI response is not a concentration signal, the refractive index increment dn/dc not being constant.

The interdetector volume correction.

The interdetector volume correction is indirectly involved here since the consequence of the flow fluctuation is an apparent peak shift. The two detectors being connected in series, the slice data acquisition is performed simultaneously on both detectors. In order to match the slice information coming from the two detectors, a correction of the viscometer slice elution volumes is performed to take into account the time necessary for each polymer molecule to move from the viscometer to the DRI.

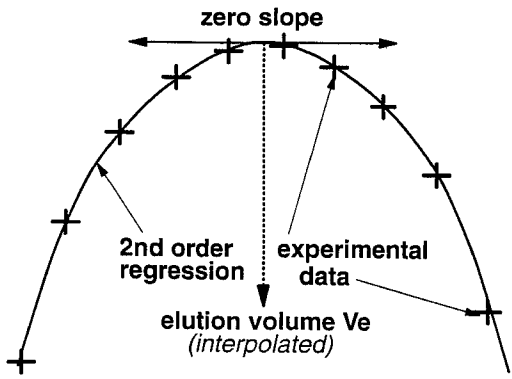

Figure 1 - Peak apex determination.

As the flow fluctuation slightly moves the viscometer downstream, this effect can be measured using the interdetector volume correction. When using an adjusted value for interdetector volume correction to obtain the appropriate value of the Mark-Houwink a exponent with a broad polymer, the difference between the theoretical value of the correction and the adjusted value corresponds to the viscometer peak shift and, consequently, to the intensity of the flow fluctuation. This is how the 100 µl apparent peak shift was measured in a standard 150 CV (1-3).

Interdetector volume determination.

In order to very carefully determine the interdetector volume, the software uses a special procedure for peak apex determination. A second order regression is performed around the highest data value, then the derivative is calculated. The exact value (interpolated) of the peak apex corresponds to the elution volume for which this derivative is equal to zero. This is represented in Figure 1.

Interdetector volume was measured using the Irganox 1010 peak that elutes around 42.5 ml with both detectors (Figure 2). This peak occurs because of the higher level of Irganox 1010 in the sample solution than in the solvent. Measuring the difference in elution volumes between the viscometer and the DRI must normally provide the interdetector volume, this molecule being assumed to be strictly monodisperse. The results obtained using a more efficient method will be published soon (9).

Interdetector volume was also measured using the PMMA standard peaks that are not strictly monodisperse; this is represented in Figure 3. A value of 95 µl

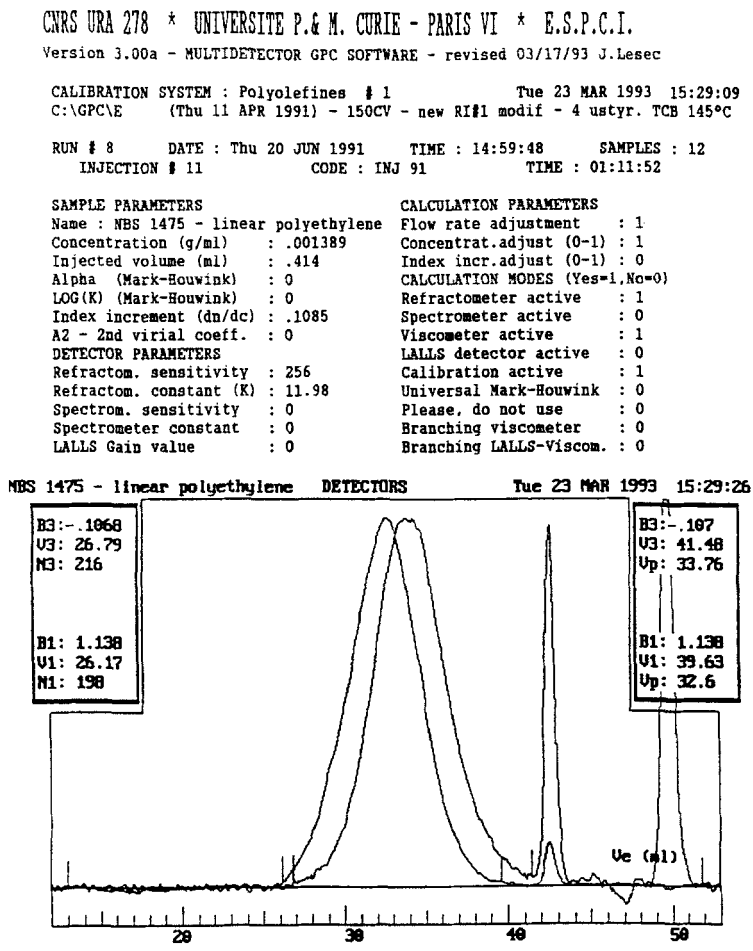

Figure 2 - Irganox 1010 peaks on a chromatogram of the NBS 1475.

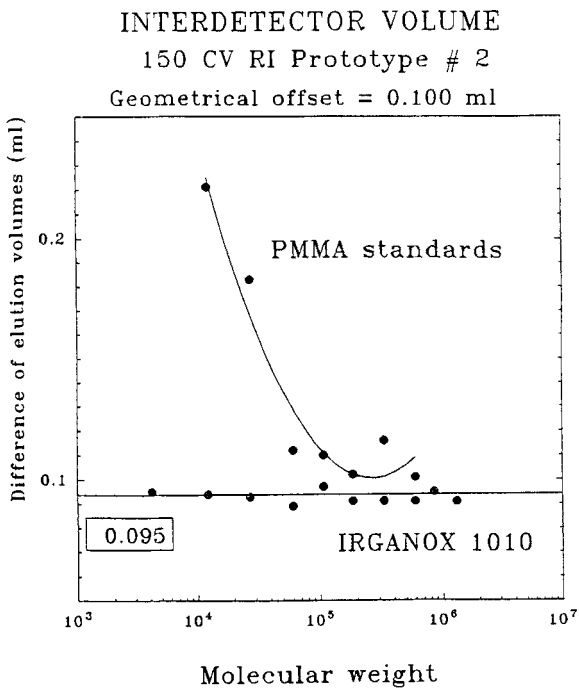

Figure 3 - Interdetector volume measured using PMMA standards and Irganox 1010 for DRI prototype #2.

was found with Irganox 1010 when the geometrical value was 100 µl, which is in very good agreement. For PMMA standards, the value is a little bit higher except for low molecular weight samples. This demonstrates that the standards are not strictly monodisperse, the low molecular weight ones exhibiting a higher polydispersity.

By comparison, the same study was run with prototype #1 and is represented in Figure 4. A value of 170 µl was found instead of the geometrical value 165 µl, which is in very good agreement, and the same behavior is observed for PMMA standards.

Polystyrene standards have also been used for the same measurements. The results are represented in Figure 5. Again, a value of 95 µl is found with Irganox 1010 but PS standards, except for the lowest and the highest molecular weight ones whose polydispersities are significantly greater than unity, exhibit an

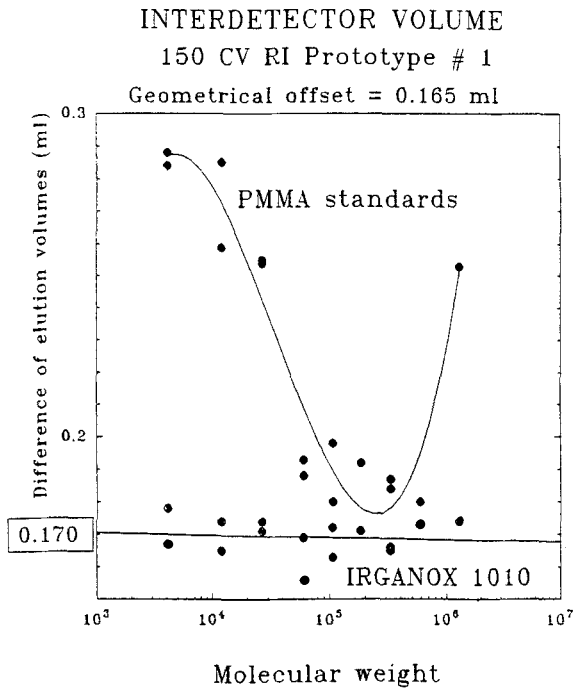

Figure 4 - Interdetector volume measured using PMMA standards and Irganox 1010 for DRI prototype #1.

abnormal behavior since they give a value a little bit smaller than Irganox 1010, which is theoretically impossible. It was not possible to find an explanation for this phenomenon. This discrepancy is extremely small and may come from a non perfect monodispersity of Irganox 1010 or a small residue of the flow fluctuation effect that was significantly weakened, but may not be completely eliminated.

In any case, these results are to be compared with the ones obtained with a standard DRI and represented in Figure 6. They were obtained at room temperature with THF using the water impurity peak to determine the interdetector volume. Again, a very good agreement was found between the geometrical volume (85 µl) and the water peak (90 µl). Conversely, the values obtained with PS standards are much smaller than expected (around 60 µl). This difference corresponds to the apparent shift of the viscometer peak downstream resulting from the flow fluctuation occurring in this unit.

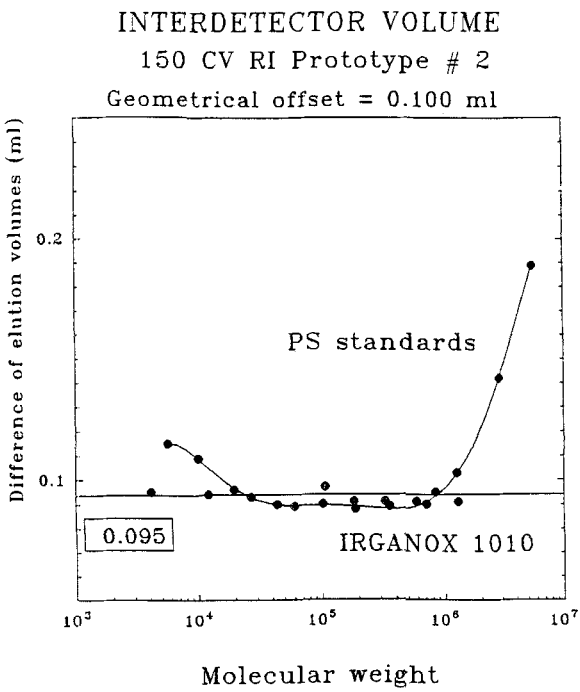

Figure 5 - Interdetector volume measured using PS standards and Irganox 1010 for DRI prototype #2.

The comparison between Figure 6 (standard DRI) and Figures 3, 4 and 5 (DRI prototypes) gives a good demonstration of the difference of behavior between a standard DRI and the DRI prototypes. It shows that the problem has been solved with the DRI prototypes and that the consequences of the flow fluctuation are eliminated.

Numerical results of polymer analysis.

Column calibration was performed with PMMA standards, using universal calibration. For this study, the combination of a LogM calibration curve and the viscosity law of standards has been used; they are represented in Figure 7. In the parameter table obtained after running the calibration and containing the analytical representation of both LogM calibration and viscosity law, it is important to note that the viscometer offset value, used to correct the

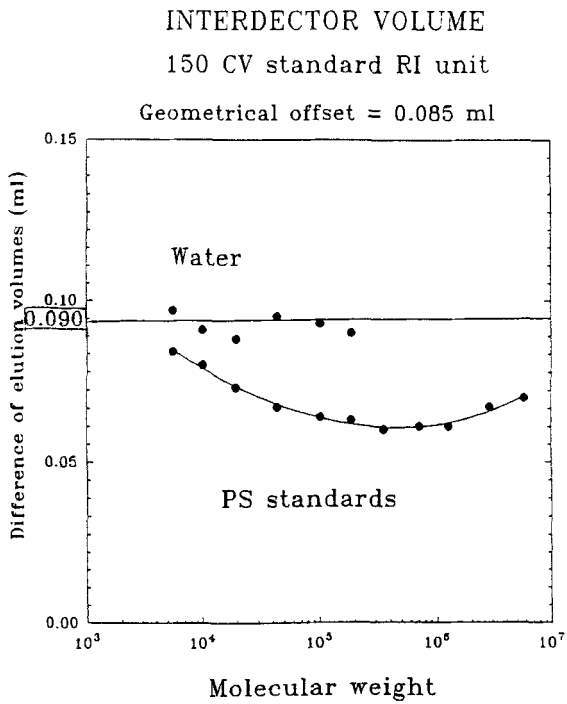

Figure 6 - Interdetector volume measured using PS standards and water peak for a standard DRI.

interdetector volume, was 85 µl. This will be discussed later. In order to check the performance of the system, several polymers were analyzed using this calibration.

Two polyethylene samples (NBS 1475 & 1476) were also studied. The chromatograms of NBS 1475, linear polymer, are represented in Figure 8 and the viscosity variations are represented in Figure 9. A very straight Mark-Houwink plot is obtained with an exponent **a** value of 0.715, which is correct. Numerical results and molecular weight distribution are represented in Figure 10. The first column of molecular weight results is in standard units (PMMA) and the second column in real units (UNIVERSAL). A value of 52,800 is found for Mw and 21,000 for Mn, which is extremely close to the expected values. The viscometer gives an intrinsic viscosity of 105 ml/g and an Mn value of 22,500, very close to the Mn value by the universal calculation.

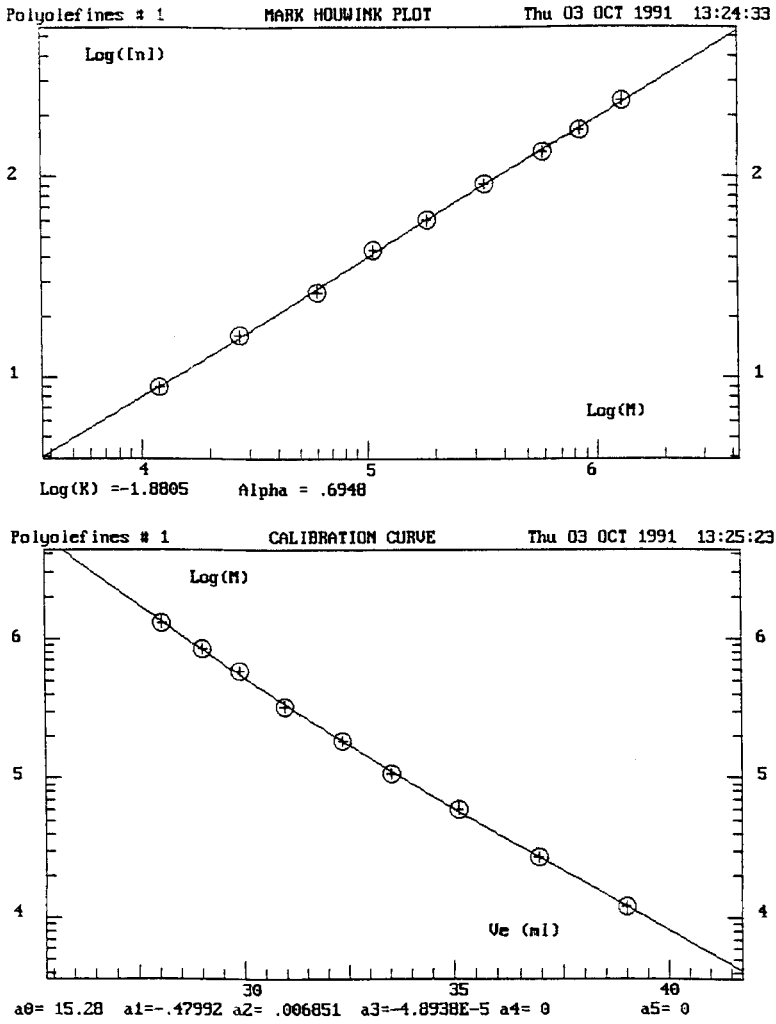

Figure 7 - Viscosity law and LogM calibration with PMMA standards.

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Version 2.20c - MULTIDETECTOR GPC SOFTWARE - revised 09/10/91 J.Lesec

CALIBRATION SYSTEM : Polyolefines # 1 Thu 03 OCT 1991 13:38:53
C:\GPC\E (Thu 11 APR 1991) - 150CV - new RI#1 modif - 4 ustyr. TCB 145°C

RUN # 15 DATE : Wed 02 OCT 1991 TIME : 17:16:51 SAMPLES : 16
INJECTION # 15 CODE : INJ 161 TIME : 07:32:59

SAMPLE PARAMETERS		CALCULATION PARAMETERS	
Name : NBS 1475		Flow rate adjustment	: 1
Concentration (g/ml)	: .002993	Concentrat.adjust (0-1)	: 1
Injected volume (ml)	: .414	Index incr.adjust (0-1)	: 0
Alpha (Mark-Houwink)	: 0	CALCULATION MODES (Yes=1,No=0)	
LOG(K) (Mark-Houwink)	: 0	Refractometer active	: 1
Index increment (dn/dc)	: .1085	Spectrometer active	: 0
A2 - 2nd virial coeff.	: 0	Viscometer active	: 1
DETECTOR PARAMETERS		LALLS detector active	: 0
Refractom. sensitivity	: 256	Calibration active	: 1
Refractom. constant (K)	: 9.22	Universal Mark-Houwink	: 0
Spectrom. sensitivity	: 0	Please, do not use	: 0
Spectrometer constant	: 0	Branching viscometer	: 0
LALLS Gain value	: 0	Branching LALLS-Viscom.	: 0

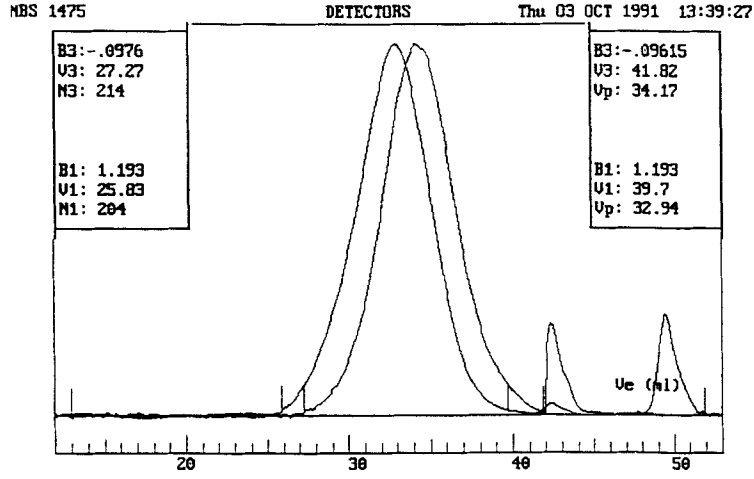

Figure 8 - Chromatograms of polyethylene NBS 1475.

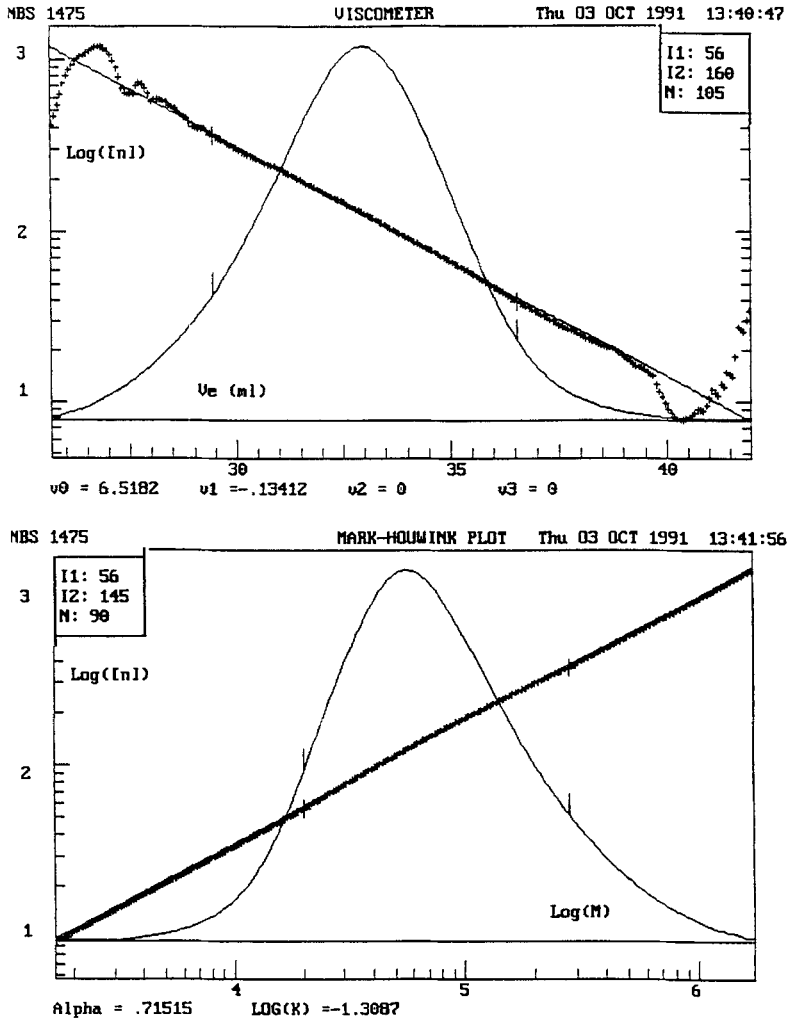

Figure 9 - Viscosity variations of polyethylene NBS 1475.

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NBS 1475                          RESULTS                  Thu 03 OCT 1991  13:42:41
  Polyolefines # 1          RUN # 15    Inj # 15          CODE : INJ 161
  DATE : Wed 02 OCT 1991    TIME : 07:32:59               Manual integration
  Calibration # 1.33        Number of points: 239         Axial dispersion: YES
MOLECULAR WEIGHTS       STANDARD   UNIVERSAL
  Peak mol. wt  Mp :     80280      32580
  Number aver.  Mn :     50520      21020
  Viscos. aver. Mv :    112800      45680
  Weight averag.Mw :    131300      52810
  Z average     Mz :    400600     159400
  Polydispersity   :      2.6         2.51
  [n] (ml/g)       :     105.4       105.6
  Log(K) (M-H)     :    -1.548      -1.309
  Alpha (M-H)      :      .707        .715
REFRACTOMETER  C/c : 1.068     Peak elution : 34.299     Baseline :-.096876
  Area constant : 1.068        Conc. (g/ml) : .0031956      dn/dc : .1085
VISCOMETER      Mn : 22500     Peak elution : 32.966     Baseline : 1.1928
  [n]area (ml/g): 105.2        [n]peak(ml/g): 125        [n]exp (ml/g): 105.2
```

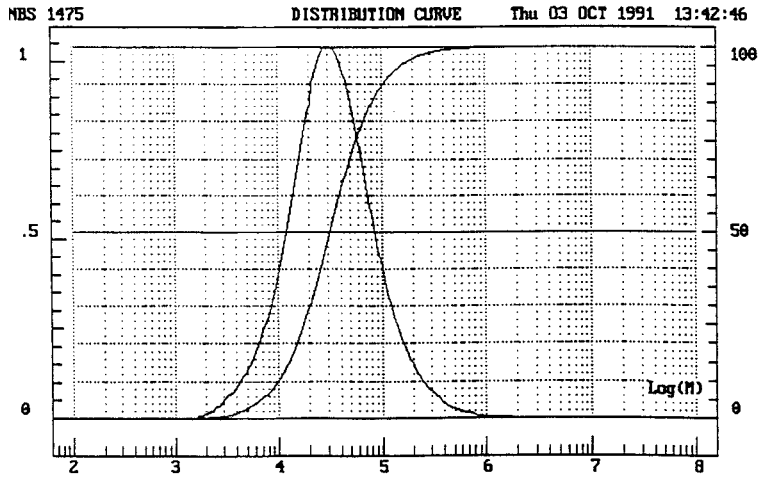

Figure 10 - Numerical results and molecular weight distribution of polyethylene NBS 1475.

The chromatograms of the branched polyethylene NBS 1476 are represented in Figure 11 and the viscosity variations in Figure 12. Contrary to the NBS 1475, the Mark-Houwink plot is curved because of branching and it is compared to the linear viscosity law obtained with the NBS 1475 (Figure 9) to provide the long-chain branching distribution $g'_i=[\eta]br_i/[\eta]lin_i$, plotted as small crosses. Figure 13 represents the numerical results and molecular weight distribution. A value of 81,300 is found for Mw and 25,800 for Mn, which is extremely close to the expected values. The viscometer gives an intrinsic viscosity of 93 ml/g and an Mn value of 29,100, close to the Mn value by the normal calculation. The average $<g'_i>$ value is found to be 0.65 with branching beginning to occur at very low molecular weight (1,600).

To check the validity of results, some broad polystyrene samples with known molecular weights (DOW 1683 and NBS 706) were also analyzed. The chromatogram of DOW 1683, linear polystyrene, is represented in Figure 14. A linear Mark-Houwink plot is obtained with an exponent value of 0.65. The "Standard" column is in PMMA units and the "Universal" column in real units. Mn and Mw were found to be 104,400 and 240,200 respectively, which is correct. The viscometer gives an intrinsic viscosity of 76.2 ml/g and an Mn value of 100,600, extremely close to the expected Mn value. Also NBS 706, represented in Figure 15 gives good values, slightly low in molecular weights: Mn=102,000, Mw=252,400. The Mark-Houwink exponent is found 0.64 (very close to the DOW value 0.65) and the viscometer gives an intrinsic viscosity of 80.7 ml/g and an Mn value of 103,700.

DISCUSSION.

All of these results where obtained with an interdetector volume correction of 85 µl instead of the 95 µl value determined using the Irganox 1010 peak (Figure 3). The reason is that this value has been adjusted with a broad linear PMMA sample to determine the exact same **a** exponent value 0.695 as with the kit of PMMA standards (Figure 7). Figure 16 represents the viscosity variations of the broad linear PMMA sample, using a correction of 85 µl, which gives the right **a** exponent 0.696. Under these conditions, the molecular weights are well calculated. The "Standard" column in PMMA units and the "Universal" column in real units are very similar, which is expected, since the sample has the same nature as the calibration standards. Again, the Mn by viscometry is found to be very close (60,550) to the "universal" value (61,930).

As a comparison, Figure 17 represents the same viscosity variations but using the Irganox 1010 correction of 95 µl which gives the underestimated value of 0.682. The difference between 0.696 and 0.682 is very small and introduces only very small variations in polymer analysis. A comparison of results obtained

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CALIBRATION SYSTEM : Polyolefines # 1 Thu 03 OCT 1991 13:44:55
C:\GPC\E (Thu 11 APR 1991) - 150CV - new RI#1 modif - 4 ustyr. TCB 145°C

RUN # 15 DATE : Wed 02 OCT 1991 TIME : 17:16:51 SAMPLES : 16
INJECTION # 16 CODE : INJ 162 TIME : 08:34:02

SAMPLE PARAMETERS		CALCULATION PARAMETERS	
Name : NBS 1476		Flow rate adjustment	: 1
Concentration (g/ml)	: .002369	Concentrat.adjust (0-1)	: 1
Injected volume (ml)	: .414	Index incr.adjust (0-1)	: 0
Alpha (Mark-Houwink)	: .71515	CALCULATION MODES (Yes=1,No=0)	
LOG(K) (Mark-Houwink)	:-1.3087	Refractometer active	: 1
Index increment (dn/dc)	: .1085	Spectrometer active	: 0
A2 - 2nd virial coeff.	: 0	Viscometer active	: 1
DETECTOR PARAMETERS		LALLS detector active	: 0
Refractom. sensitivity	: 256	Calibration active	: 1
Refractom. constant (K)	: 9.22	Universal Mark-Houwink	: 0
Spectrom. sensitivity	: 0	Please, do not use	: 0
Spectrometer constant	: 0	Branching viscometer	: 1
LALLS Gain value	: 0	Branching LALLS-Viscom.	: 0

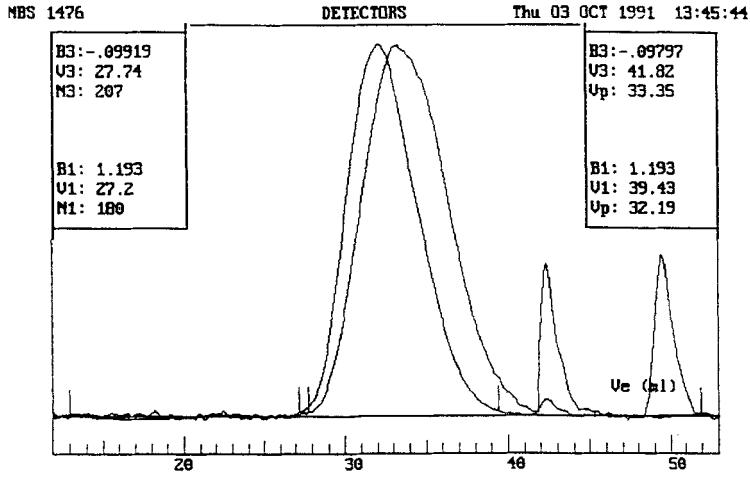

Figure 11 - Chromatograms of polyethylene NBS 1476.

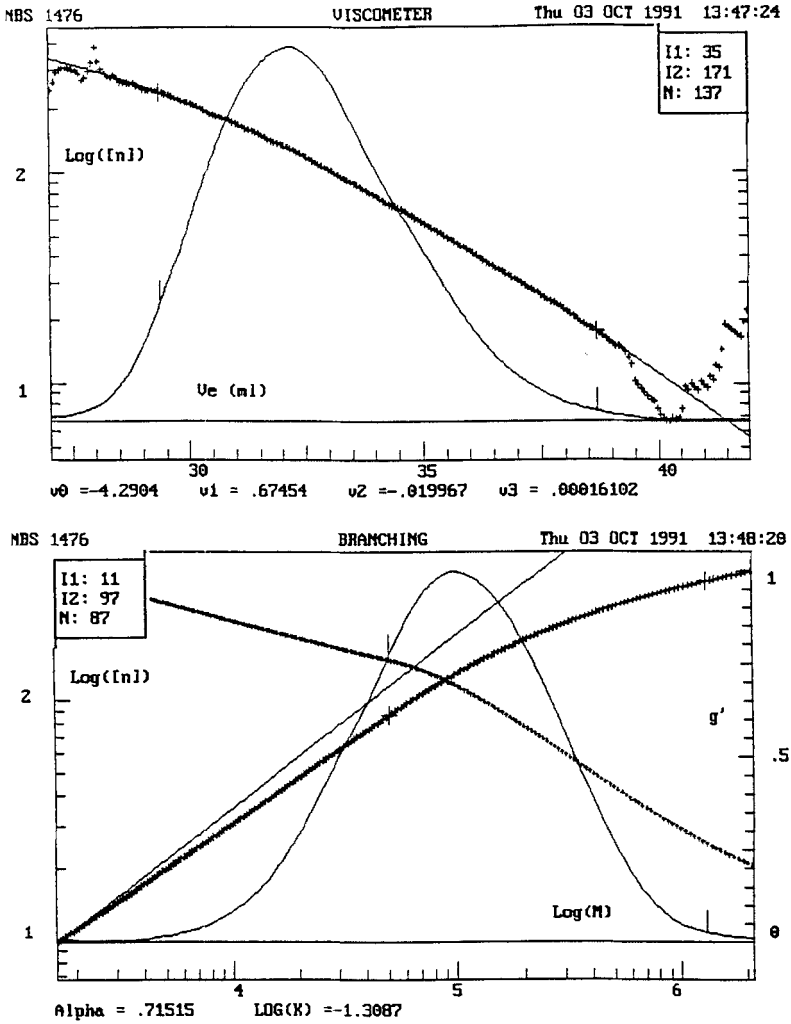

Figure 12 - Viscosity variations of polyethylene NBS 1476.

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NBS 1476		RESULTS		Thu 03 OCT 1991 13:49:10
Polyolefines # 1		RUN # 15	Inj # 16	CODE : INJ 162
DATE : Wed 02 OCT 1991		TIME : 08:34:02		Manual integration
Calibration # 1.33		Number of points: 219		Axial dispersion: YES
MOLECULAR WEIGHTS	STANDARD	UNIVERSAL	g'BRANCH.	
Peak mol. wt Mp :	124000	50050	.751	
Number aver. Mn :	56470	25770	.8	
Viscos. aver. Mv :	119700	69290	.732	
Weight averag.Mw :	151600	81340	.714	
Z average Mz :	332700	234300	.547	
Polydispersity :	2.68	3.16	< g' > :	
[n] (ml/g) :	98.83	142.3	.654	
Log(K) (M-H) :	-.4474	-1.309	g' mass:	
Alpha (M-H) :	.481	.715	1643	
REFRACTOMETER C/c : .9772		Peak elution : 33.276		Baseline :-.098578
Area constant : .9775		Conc. (g/ml) : .0023149		dn/dc : .1085
VISCOMETER Mn : 29090		Peak elution : 32.148		Baseline : 1.1928
[n]area (ml/g): 91.84		[n]peak(ml/g): 128.3		[n]exp (ml/g): 93.03

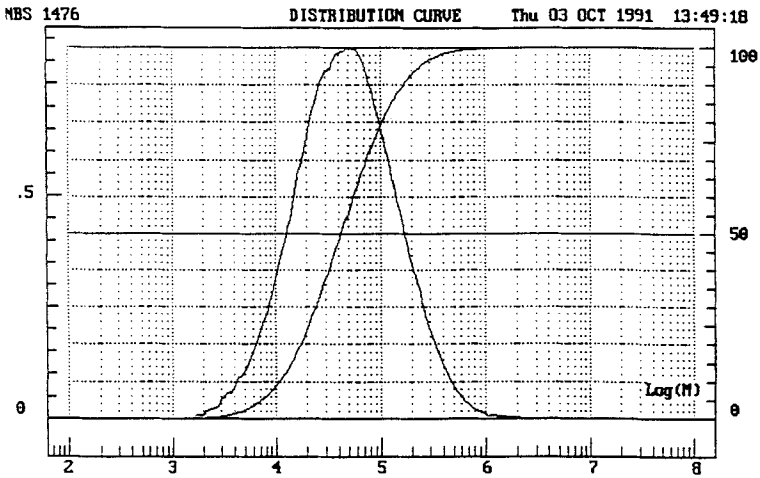

Figure 13 - Numerical results and molecular weight distribution of polyethylene NBS 1476.

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DOW 1683 - 3	RESULTS		Thu 03 OCT 1991 16:28:49
Polyolefines # 1	RUN # 15	Inj # 12	CODE : INJ 158
DATE : Wed 02 OCT 1991	TIME : 04:29:51		Manual integration
Calibration # 1.33	Number of points: 182		Axial dispersion: YES

MOLECULAR WEIGHTS	STANDARD	UNIVERSAL
Peak mol. wt Mp :	190800	173200
Number aver. Mn :	117300	104400
Viscos. aver. Mv :	229500	210400
Weight averag.Mw :	258300	240200
Z average Mz :	484400	467700
Polydispersity :	2.2	2.3
[n] (ml/g) :	76.59	76.85
Log(K) (M-H) :	-1.701	-1.583
Alpha (M-H) :	.669	.652

REFRACTOMETER C/c : .9987	Peak elution : 32.283		Baseline :-.12113
Area constant : .5414	Conc. (g/ml) : .0016379		dn/dc : .0588
VISCOMETER Mn : 100600	Peak elution : 30.961		Baseline : 1.1927
[n]area (ml/g): 74.63	[n]peak(ml/g): 99.44		[n]exp (ml/g): 76.17

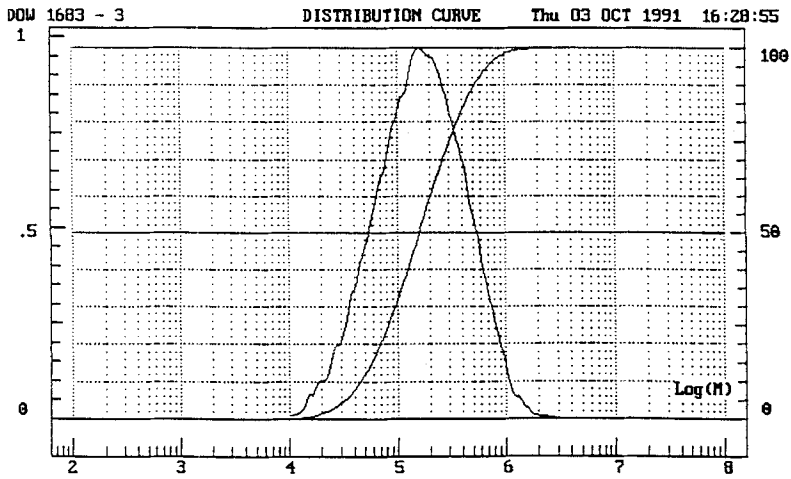

Figure 14 - GPC analysis of broad polystyrene DOW 1683.

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NBS 706 - 3	RESULTS		Thu 03 OCT 1991 16:33:39
Polyolefines # 1	RUN # 15	Inj # 13	CODE : INJ 159
DATE : Wed 02 OCT 1991	TIME : 05:30:53		Manual integration
Calibration # 1.33	Number of points: 203		Axial dispersion: YES

MOLECULAR WEIGHTS	STANDARD	UNIVERSAL
Peak mol. wt Mp :	243300	220100
Number aver. Mn :	117400	102000
Viscos. aver. Mv :	246400	223800
Weight averag.Mw :	273600	252400
Z average Mz :	462100	442400
Polydispersity :	2.33	2.48
[n] (ml/g) :	81.08	81.28
Log(K) (M-H) :	-1.655	-1.51
Alpha (M-H) :	.661	.639

REFRACTOMETER C/c : 1.012	Peak elution : 31.733		Baseline :-.11949
Area constant : .5484	Conc. (g/ml) : .0017864		dn/dc : .0588
VISCOMETER Mn : 103700	Peak elution : 30.906		Baseline : 1.1926
[n]area (ml/g): 79.94	[n]peak(ml/g): 102.2		[n]exp (ml/g): 80.75

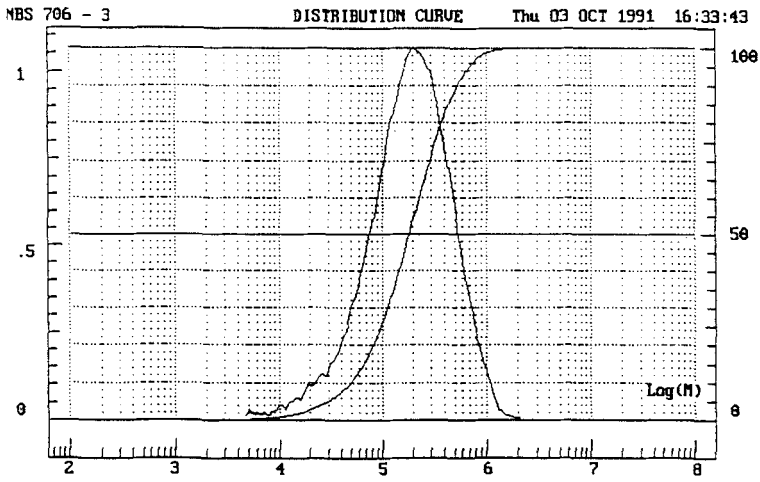

Figure 15 - GPC analysis of broad polystyrene NBS 706.

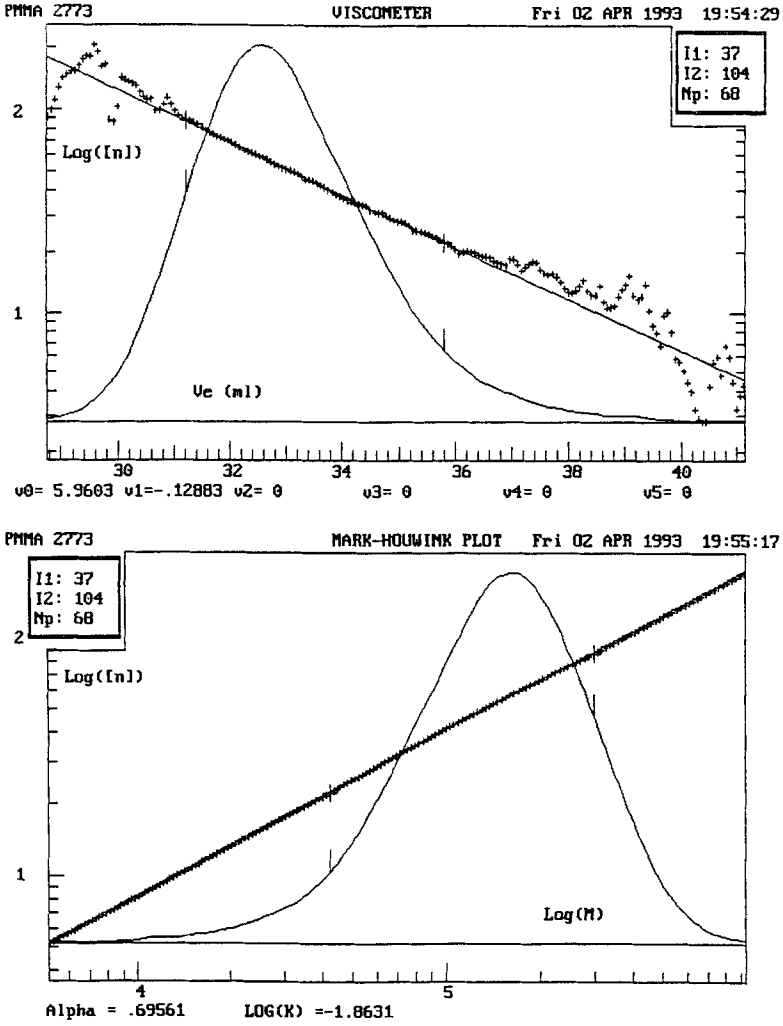

Figure 16 - Viscosity variations of a broad PMMA using 85 µl.

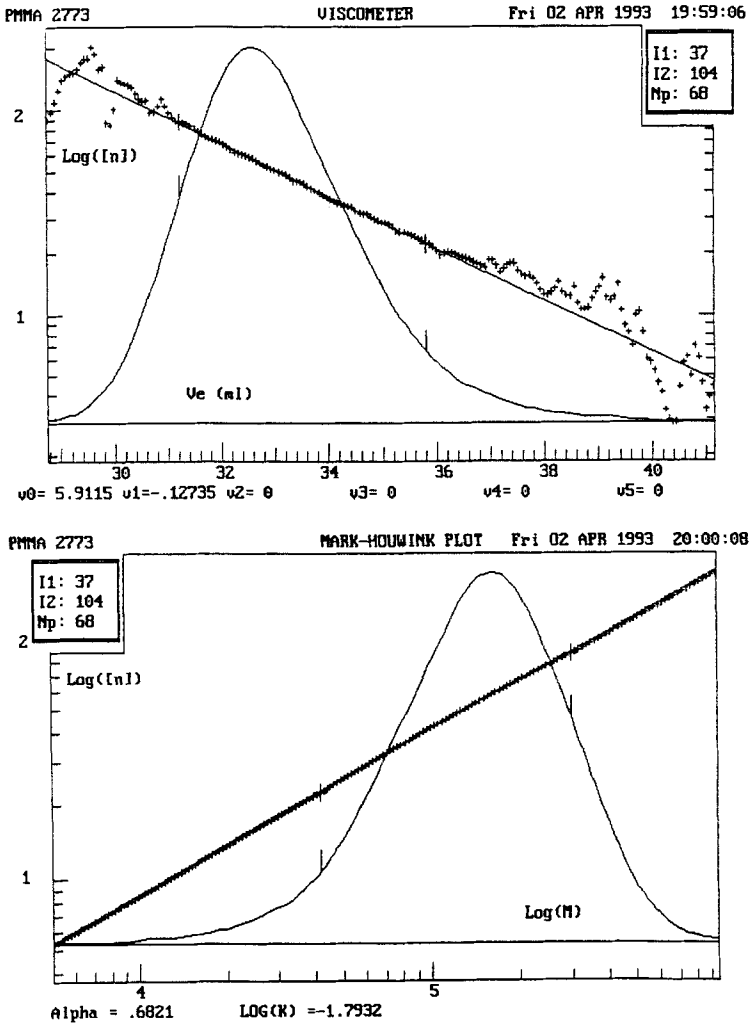

Figure 17 - Viscosity variations of a broad PMMA using 95 µl.

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PMMA 27000 * 2	RESULTS		Fri 02 APR 1993 20:06:18
Polyolefines # 1	RUN # 14	Inj # 3	CODE : INJ 133
DATE : Tue 01 OCT 1991	TIME : 19:54:56		Manual integration
Calibration # 1.33	Number of points: 85		Axial dispersion: YES

MOLECULAR WEIGHTS	STANDARD	UNIVERSAL
Peak mol. wt Mp :	27120	26090
Number aver. Mn :	23870	22540
Viscos. aver. Mv :	25870	24770
Weight averag.Mw :	26290	25320
Z average Mz :	28280	27590
Polydispersity :	1.1	1.12
[n] (ml/g) :	16	16
Log(K) (M-H) :	-1.443	-1.203
Alpha (M-H) :	.6	.548

REFRACTOMETER C/c : 1	Peak elution : 36.944	Baseline :-.10396
Area constant : .3006	Conc. (g/ml) : .001814	dn/dc : .0307
VISCOMETER Mn : 21480	Peak elution : 36.839	Baseline : 1.1905
[n]area (ml/g): 16.19	[n]peak(ml/g): 16.83	[n]exp (ml/g): 16

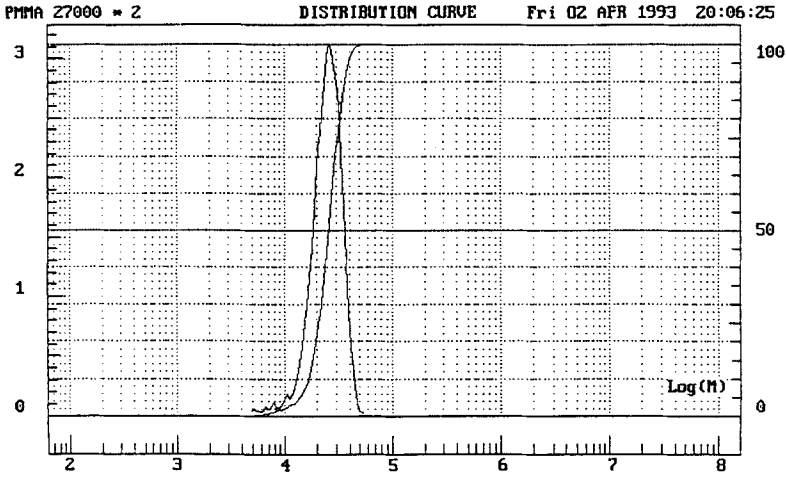

Figure 18 - GPC analysis of PMMA standard 27,000 using 85 µl.

Table 1-Comparison of NBS 1475 and 1476 values using either 85 µl or 95 µl.

	1475(85µl)	1475(95µl)	1476(85µl)	1476(95µl)
Mn	21,020	20,970	25,770	25,290
Mw	52,810	52,340	81,340	81,300
[η]	105.2	105.3	93.03	92.9
a	0.715	0.710	-	-
LogK	-1.309	-1.2876		
<g'>	-	-	0.654	0.652

using either 85 µl or 95 µl for interdetector volume correction is given in Table 1 for NBS 1475 and 1476.

These differences are very small and quite negligible on broad polymers; only the viscosity law coefficients change slightly. For narrow polymers, this change is more significant. Figure 18 represents the analysis of the PMMA standard 27,000 using 85 µl. Both "standard" and "universal" columns are quite identical and the determination of molecular weights is good. The Mark-Houwink a exponent was found 0.55, different from the calibration value 0.695 (Figure 7), but, still an acceptable value for a standard since band broadening occurs. By comparison, when using 95 µl, the exponent value decreases from 0.55 to 0.46 which shows that narrow standards are much more sensitive to the correction. They may be used to carefully adjust the interdetector offset, but a very accurate band broadening correction has to be used.

The system has also been checked with polystyrene standards. Polystyrene samples are very sensitive to chemical degradation in TCB; the solutions need to be very well protected by Irganox 1010 and also against degradation by light. When the proper precautions are not taken, degradation may occur and this is probably the reason for underestimated values obtained with DOW 1683 and NBS 706 (Figures 14 and 15). A single universal calibration curve was obtained using the two sets of standards (PS + PMMA) and is plotted in Figure 19. There is excellent agreement between both sets of standards, which shows that the system was running well.

CONCLUSION.

The performance of the DRI prototype #2 is excellent. The changes in internal geometry correct for the occurrence of the flow fluctuation and its consequences when the polymer solution flows across the detectors. Contrary to the previous experiments using a standard DRI, where a peak shift of 100 µl was observed, the difference between the measured interdetector volume using

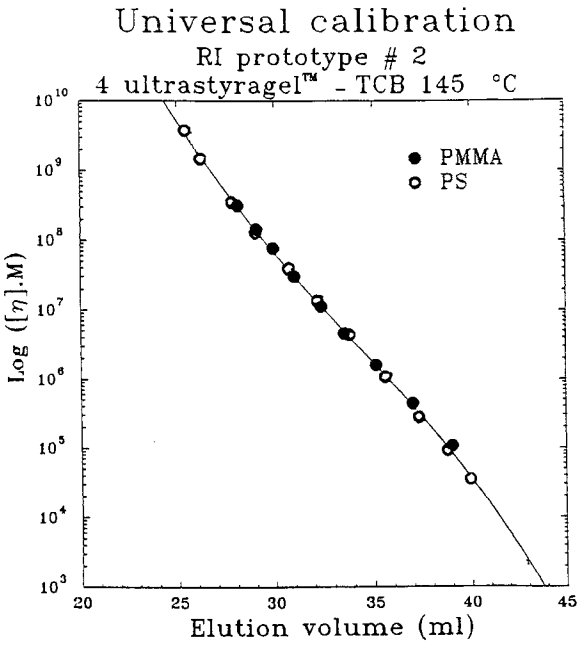

Figure 19 - Single Universal calibration with PS and PMMA standards.

Irganox 1010 (95 µl) and the adjusted value (85 µl), to obtain exactly the same Mark-Houwink exponent with a set of standards and with a broad sample with the same chemical nature, is very small (10 µl).

The interpretation of this 10 µl value is very difficult since this is, at least, the experimental error on interdetector volume measurement using Irganox 1010 and also the experimental error when adjusting the Mark- Houwink exponent with a broad sample on the set of standards. This small discrepancy may come from a very weak residual flow fluctuation but the experimental errors do not allow conclusive explanation.

Anyway, this very weak difference does not introduce any significant error on results. Table 1 shows only very minor changes in molecular weights and other parameters when using either 95 µl or 85 µl for interdetector volume correction. Even the Mark-Houwink exponent variation, which is at the origin of this study and of the DRI prototype design, does not vary significantly (from 0.710 to 0.715). The discrepancy value 10 µl is probably the extreme limit of precision we can expect experimentally, even under the best conditions, and it certainly has no physical meaning.

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