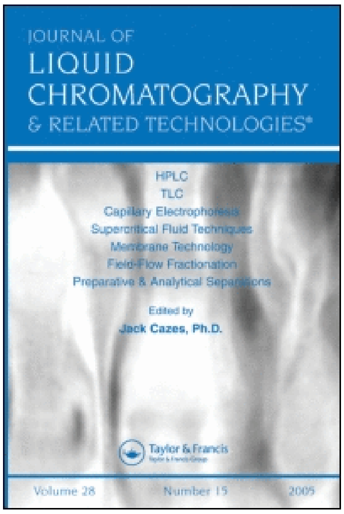

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Data Treatment in Aqueous GPC with On-Line Viscometer and Light Scattering Detectors

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DATA TREATMENT IN AQUEOUS GPC WITH ON-LINE VISCOMETER AND LIGHT SCATTERING DETECTORS

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ABSTRACT

Gel Permeation Chromatography (GPC) is becoming a very powerful tool for polymer characterization with the coupling of mass detectors using viscometry and light scattering techniques. The triple coupling seems to be the best way since the light scattering detector gives absolute molecular weights and viscometric detection provides intrinsic viscosity, leading to absolute molecular weights through universal calibration and information on long-chain branching. However, instrumentation becomes more sophisticated, expensive and, simultaneously, very sensitive to several parameters which are not critical in classical GPC. Moreover, an on-line computer is required for data acquisition and appropriate software for reliable interpretation of chromatograms.

Our experiments were performed with a Waters Associates room temperature instrument in which a home-made continuous viscometer, using pressure transducers, and a light scattering detector (LALLS Chromatix-CMX 100) were inserted on-line between the column set and the refractometer. Data were interpreted through personal software written on HP9836 and PC-AT computers.

We describe, here, the behavior of some polymers in aqueous solutions, mainly those that are commonly used as calibration standards (polyethylene oxides, pullulans). Experiments were run using two different sets of columns ('Ultrahydrogel' from Waters Associates and 'Shodex OH-Pak' from Showa Denko K.K.) in several aqueous solvents, pure water or water with various salts ($LiNO_3$, $NaNO_3$, LiCl, NaCl, Na_2SO_4) at different concentrations. Intrinsic viscosities were determined through viscometric detection and weight average molecular weights through the LALLS detector, leading to a plot of universal calibration curves Log([η].M) versus elution volumes.

INTRODUCTION

Introduction of universal calibration by Benoît et al. in 1966 (1) evidenced the need for viscometric detection. Such a detector, compatible with modern GPC columns, was first described by Ouano in 1972 (2). On this basis, several viscometers were studied in different laboratories (3-12) and now, two models are commercially available from Viscotek (13) and Waters Associates (14,15). At the same time, the low-angle laser light scattering (LALLS) technique was introduced by Ouano and Kaye in 1974 (16,17) and developed by Chromatix (18) and recently, a new multi-angle light scattering technique has been commercialized by Wyatt Technology Corp. (19).

However, in spite of its great interest, the current practice of mass detector coupling is recent. These couplings bring forward to Gel Permeation Chromatography (GPC) a high capacity for characterization by comparison with classical GPC using a concentration detector only, which provides relative information. The interest of the triple coupling is that molecular weights can be determined through two different and independant ways. The viscometric detector provides intrinsic viscosity and, consequently, absolute molecular weights through universal calibration and light scattering detection gives absolute molecular weights without the need of calibration. However, these two complementary techniques, when coupled to GPC, make the instrumentation very sophisticated, expensive and difficult to handle, since it is tremendously sensitive to several parameters which are not critical in traditional GPC, such as concentration, perfect control of flow rate, solvent purity, etc... Moreover, the only way to take advantage of this multiple information is the connection of detectors with an on-line microcomputer for automatic data acquisition and appropriate software for reliable interpretation of chromatograms.

For aqueous GPC, mechanisms are often complex and interference between the size exclusion mechanism and other mechanisms can occur. The triple coupling viscometer-LALLS-refractometer provides multiple information and, therefore, allows the detection of abnormal polymer behavior. We report here some results of aqueous polymer characterization and some problems concerning calibration of the column set and concentration effects.

EXPERIMENTAL

A room-temperature instrument was used for this study and is described in Figure 1. It is composed of the following components:

- Micropump prepump (Cole-Parmer, Chicago, Ill.), to ensure perfect running of the main pumping system in water,
- M 6000 A pumping system (Waters Assoc, Milford, Ma.),
- 7010 injector with a 200-μL loop (Rheodyne, Calif.),
- R-401 differential refractometer (Waters Associates).

Viscometer and light scattering detectors were inserted 'on-line' between the outlet of the column set and the inlet of the

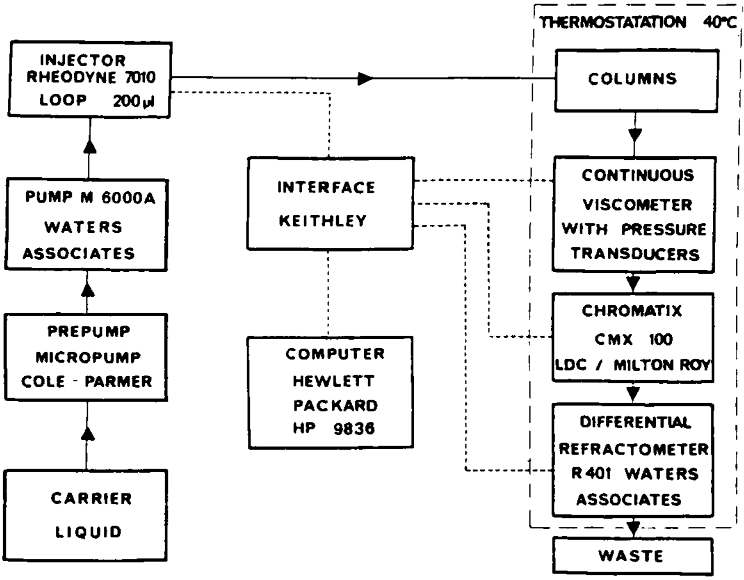


Figure 1. General scheme of the GPC instrument.

differential refractometer, in that order. Every component is kept at a well-controlled temperature of 40°C. The three detectors are connected to a microcomputer (HP 9836 or PC-AT) through a Keithley interface for data collection.

Viscometer : This is a home-made continuous viscometer (5,6) using two Sedeme (Paris, France) pressure transducers (CMAC 5 range: 5 bars) and a 3-m long Teflon capillary (0.3 mm I.D.) (11,12). This device has been recently improved (14,15) by the use of a differential pressure transducer with a lower range (5 KPA) and a much shorter capillary (6 inches) with a greater internal diameter (14/1000 inch) which leads to smaller internal volume and shear rate. It is now included in the new Waters Associates instrument, GPC 150CV.

Light scattering detector : The instrument used is a Chromatix CMX 100 (LALLS - LDC Milton Roy). It uses a He-Ne laser (632.8 nm) and measures the scattered light between 5 and 6°. A Millipore filter (0.22 µm) is inserted between columns and detectors to ensure proper clarification of eluates before the detector inlet.

Column sets : Two sets of columns were used: Ultrahydrogel 500, 1000 and 2000 Å (Waters Associates), and Shodex OH-pak B803, B804, B805 and B806 (Showa Denko, Tokyo,Japan). Mobile phases consisted of pure water or water with different salts ($LiNO_3$, $NaNO_3$, NaCl, LiCl, Na_2SO_4) at variable concentrations (0.1M - 0.5M). In every case, 400 ppm of NaN_3 was added to the mobile phase to prevent biological degradation.

<u>*Calibration standards*</u> : Two sets of standards were used: polyethylene oxide (20,000-860,000) from Toyo Soda and pullulan polysaccharide (7,000-900,000) from Showa Denko.

<u>*Data acquisition*</u> : A Keithley interface (Cleveland, Ohio) (either the couple scanner 705 and multimeter 195 or the scanner-multimeter 199) was used to perform analog to digital conversion. These components are connected through a IEEE-488 interface to the microcomputer. Two different microcomputers with custom-made software were used:

- A Hewlett-Packard HP 9836 with dual detection software GPC-VISCO and GPC-LALLS supporting only one mass detector (viscometer or LALLS) coupled with the refractometer.

- A PC-AT computer with a 'Multidetector GPC Software' capable of monitoring three simultaneous detectors selected among four: refractometer, spectrometer, viscometer and light scattering detector.

RESULTS AND DISCUSSION

<u>*PRINCIPLE OF DATA TREATMENT.*</u>

The interest of viscometer-LALLS-refractometer triple detection is to obtain three different and independant sets of information for the polymer. A typical representation is given in Figure 2, where the three signals are plotted full scale as a function of elution volume, where Bx is the baseline value at volume Vx, Nx is the total number of points (with x=3: refractometer, x=2: viscometer and x=1: light scattering detector), and Vp is the elution volume at the peak apex. Although mass detector signals were corrected for their physical offset volume from the refractometer, the three peaks do not overlap because of the different kind of response. At a given elution volume:

- the refractometer gives: $R_i=K_R \cdot dn/dc \cdot C_i$ where
  - K_R is the refractometer constant (obtained by calibration),
  - C_i is the polymer concentration,
  - dn/dc is the refractive index increment.
  - Peak integration provides dn/dc of the polymer.

- the light scattering detector gives: $L_i=K_L \cdot C_i \cdot M_i$ where
  - K_L is the detector constant containing several parameters such as dn/dc and calibration constants,
  - M_i is the absolute molecular weight.
  - Peak integration provides weight-average molecular weight $\overline{M_w}$.

- the viscometer gives: $V_i=K_v \cdot C_i \cdot [\eta_i]$ where
  - K_v is the viscometer constant ($k_v \# P_0$, viscometer baseline),
  - $[\eta_i]$ is the polymer intrinsic viscosity, (calculations described in details in (11)).
  - Peak integration provides the polymer intrinsic viscosity $[\eta]$.

The procedure of data handling is described in (20). We have represented, in Figure 3, the light-scattering detector signal where the logarithm of molecular weight from the light scattering calculation is

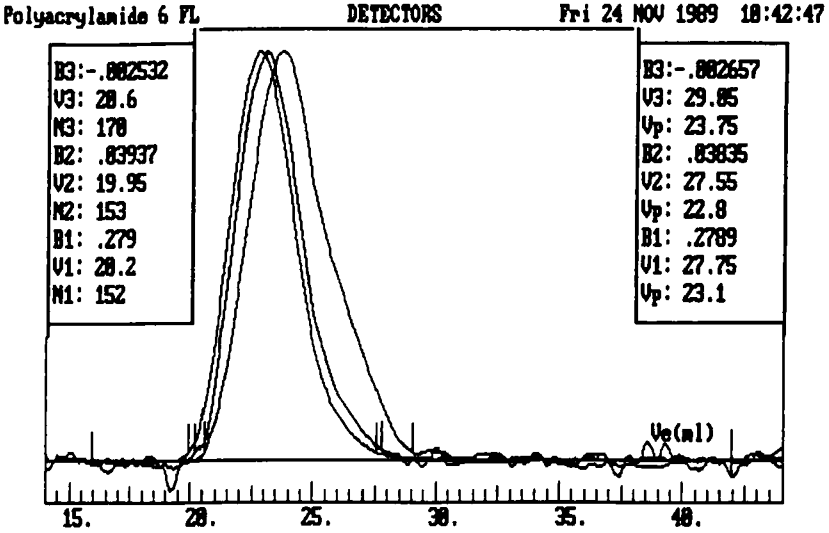


Figure 2. Chromatograms of a polymer using triple detection, from left to right: LALLS, viscometer and refractometer.

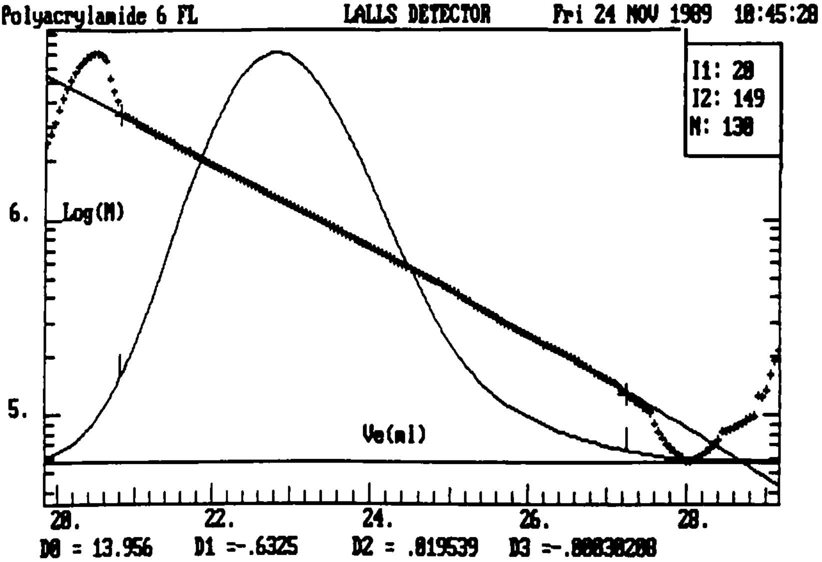


Figure 3. Light scattering data representation.

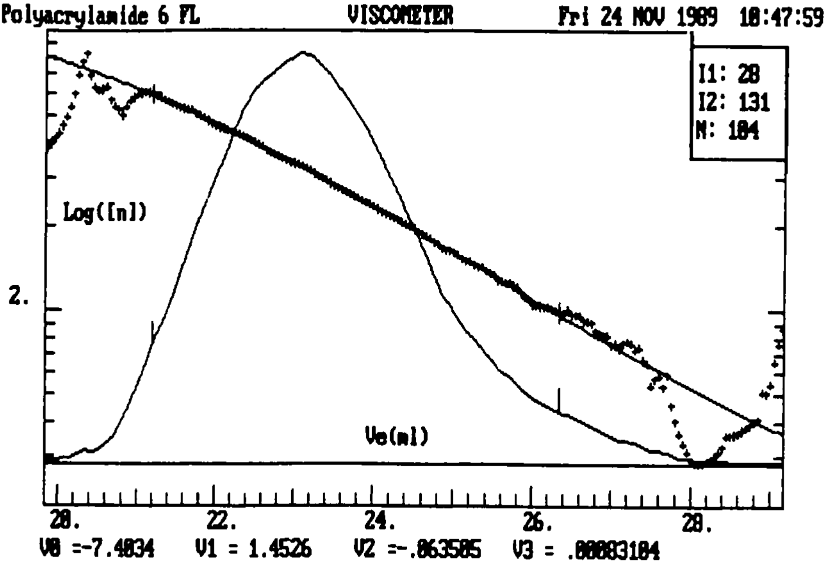


Figure 4. Viscometric data representation.

plotted versus elution volume. Extrapolation of signal outside the reliable part of data is performed by a 3^{rd}-degree polynomial least-square regression. The same procedure is applied to viscometric data and is described in Figure 4 where the viscometric signal is represented and the logarithm of intrinsic viscosity is plotted versus elution volume. After these data reduction procedures, data handling is much easier. As an example, we have represented, in Figure 5, the viscometer signal and the plot of the logarithm of intrinsic viscosity versus the logarithm of molecular weight. A straight line is typically obtained, characteristic of the Mark-Houwink relationship. In this particular case, the polymer is linear and, accordingly, a 1^{st}-degree least-square regression provides both alpha and K Mark-Houwink coefficients. For long-chain branched polymers, the procedure is more complicated, since the viscosity law is generally curved, but leads to the long-chain branching distribution g' by comparison with the corresponding linear polymer viscosity law.

CALCULATION OF MOLECULAR WEIGHTS.

The different absolute average molecular weights ($\overline{M_n}$, $\overline{M_v}$, $\overline{M_w}$, and $\overline{M_z}$) are calculated through the classical slicing procedure but, contrary to classical GPC, the amount of material injected into the column set is used in calculations. Consequently, sample concentration and injection volume must be known precisely. Three different ways are available for molecular weight calculation as shown in Figure 6.

- The classical GPC calculation requires a calibration by narrow distribution standards Log(M)=f(Ve) and provides relative molecular

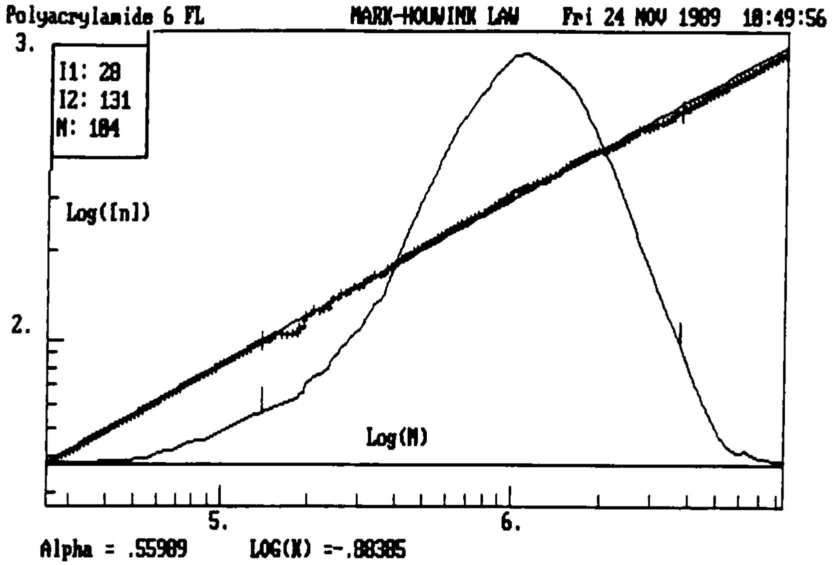
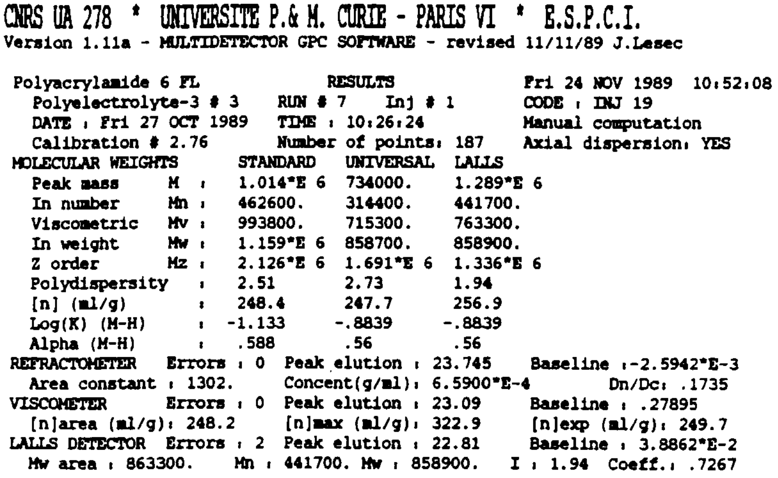


Figure 5. Mark-Houwink relationship representation.



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CNRS UA 278  *  UNIVERSITE P.& M. CURIE - PARIS VI  *  E.S.P.C.I.
Version 1.11a - MULTIDETECTOR GPC SOFTWARE - revised 11/11/89 J.Lesec

 Polyacrylamide 6 FL                RESULTS              Fri 24 NOV 1989  10:52:08
   Polyelectrolyte-3 # 3    RUN # 7    Inj # 1          CODE : INJ 19
   DATE : Fri 27 OCT 1989   TIME : 10:26:24             Manual computation
   Calibration # 2.76       Number of points: 187       Axial dispersion: YES
 MOLECULAR WEIGHTS          STANDARD    UNIVERSAL   LALLS
   Peak mass       M  :     1.014*E 6   734000.     1.289*E 6
   In number       Mn :     462600.     314400.     441700.
   Viscometric     Mv :     993800.     715300.     763300.
   In weight       Mw :     1.159*E 6   858700.     858900.
   Z order         Mz :     2.126*E 6   1.691*E 6   1.336*E 6
   Polydispersity     :     2.51        2.73        1.94
   [n] (ml/g)         :     248.4       247.7       256.9
   Log(K) (M-H)       :    -1.133      -.8839      -.8839
   Alpha (M-H)        :     .588        .56         .56
REFRACTOMETER   Errors : 0  Peak elution : 23.745    Baseline :-2.5942*E-3
  Area constant : 1302.     Concent(g/ml): 6.5900*E-4         Dn/Dc: .1735
VISCOMETER      Errors : 0  Peak elution : 23.09     Baseline : .27895
  [n]area (ml/g): 248.2     [n]max (ml/g): 322.9     [n]exp (ml/g): 249.7
LALLS DETECTOR  Errors : 2  Peak elution : 22.81     Baseline : 3.8862*E-2
  Mw area : 863300.     Mn : 441700. Mw : 858900.    I : 1.94  Coeff.: .7267
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Figure 6. Results of molecular weight calculations.

weights in MW units of the standards used. (column '*STANDARD*' in Figure 6).

- The second way is universal calculation using alpha and K coefficients of the Mark-Houwink relationship of standards used for calibration. It requires viscometric data which give experimental viscosity law coefficients (Figure 5) and provides absolute molecular weights by viscometric conversion of '*STANDARD*' values (column '*UNIVERSAL*' in Figure 6). This way is completely equivalent but more flexible than the use of a universal calibration curve Log([η].M)=f(Ve). Moreover, for long-chain branched polymers, long-chain branching information is obtained by comparison, at every molecular weight, between experimental viscosity law and the one of the corresponding linear polymer. Long-chain branching distribution g'(M) can thus be determined (5-11).

- The third way uses light scattering data to provide absolute molecular weights (column '*LALLS*' in Figure 6) without the need of any calibration. The refractive index increment dn/dc, used in light scattering equations, is determined through refractometric data if the refractometer constant has been accurately calibrated.

The advantage of this dual calculation of absolute molecular weights is that each one should provide the correct values independently. When agreement between the two sets of values is correct, we can consider that numerical values are accurate and that the GPC system is running perfectly with well-controlled parameters. Conversely, when the discrepancy is greater than the usual error, this indicates poor behavior of the GPC system with multiple origins. Poor control of the injected amount of material can lead to a significant discrepancy. A small variation of eluant flow rate can lead to an unappropriate reference in the calibration curve; however, the use of an in-line continuous viscometer allows for perfect monitoring of flow rate with excellent accuracy. But the main origin, especially for aqueous polymers, is the appearance of additional retention mechanisms, different from size exclusion, which generally increases elution volumes, leading to a tremendous decrease of '*UNIVERSAL*' molecular weights.

COLUMN CALIBRATION IN PURE WATER.

In order to calibrate our two GPC column sets, consisting of Ultrahydrogel 500, 1000 and 2000 Å and Shodex OH-pak B803, B804, B805 and B806, two sets of different standards were used: polyethylene oxide (20,000-850,000) and pullulan polysaccharide (7,000-900,000). Calibration curves are represented in Figure 7 and in Figure 8, respectively. Obviously, a tremendous discrepancy is observed between the two sets of standards. Although both curves look close together and, as a logarithmic scale is used for molecular weights, there is a factor of approximately two between values obtained through both calibrations. These results lead to the question: **Is universal calibration valid in water or is there any problem with our experiments ?**

Hopefully, universal calibration has been widely demonstrated, so our experimental conditions were carefully checked in order to determine the origin of this discrepancy. In fact, calibration was performed by a classical procedure, which consists of injecting calibration standards with decreasing concentrations as molecular weight

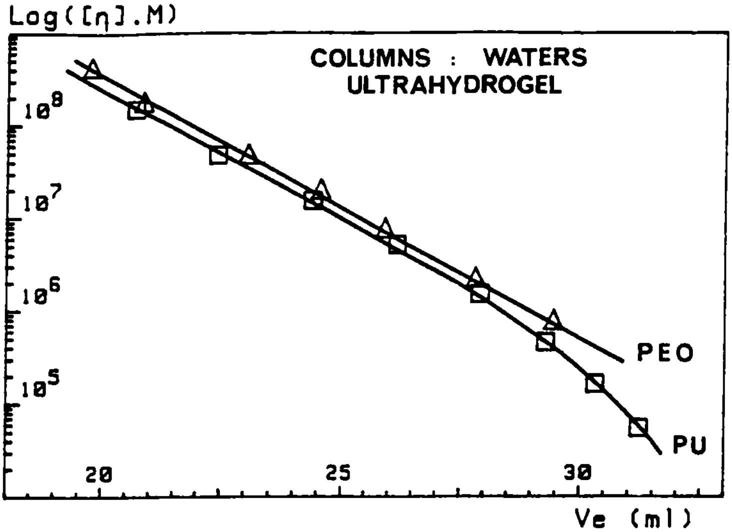

Figure 7. Universal calibration curves in pure water.
Columns: Ultrahydrogel - (□) pullulan, (△) polyethylene oxide.

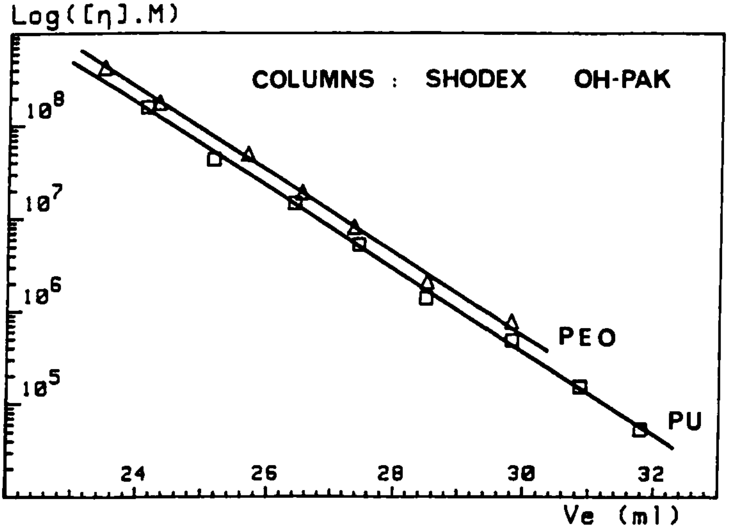

Figure 8. Universal calibration curves in pure water.
Columns: Shodex OH-pak - (□) pullulan, (△) polyethylene oxide.

increases, the same rule being applied for both sets of standards (C*M = 600), except for low molecular weight compounds for which it is not possible to increase the solute concentration too much.

The problem comes from the intrinsic viscosities of polyethylene oxides which are approximately three times higher that those of pullulan standards at the corresponding molecular weights. This means that, in our experimental conditions, the [η]*C parameter was 0.16 for pullulan standards when [η]*C was 0.5 for polyethylene oxides. Now, it is well-known that concentration effects are in relation with absolute viscosity of eluates (21,22) which is well-represented by the [η]*C parameter. Let us point out that the [η]*C parameter represents also the viscometer response, as previously described.

These concentration effects were checked by injecting standards at different concentrations and by extrapolating elution volumes at zero concentration. Figures 9 and 10 represent universal calibration curves at zero concentration for Ultrahydrogel and Shodex OH-pak columns, respectively, for both sets of standards. For each standard, values at zero concentration (the smallest elution volume) and at [η]*C=0.16 (the highest elution volume) are represented. They do not overlap exactly, which means that a small concentration effect occurs even at [η]*C=0.16, accordingly at [η]*C=0.5 which were the injection conditions for polyethylene oxide standards in Figure 7 and 8. Therefore, the discrepancy between the two sets of standards disappears when lowest injection concentration is used, that demonstrates that the difference between calibration curves in Figures 7 and 8 is really due to concentration effects.

It is important to point out that, although the [η]*C parameter has no dimension when using [η] in mL/g and C in g/mL, its value depends upon column volume and injection volume. Our units correpond to a set of 3 or 4 classical GPC columns and an injection volume of 200µL. In our experiments, a value 0.16 was used in order to obtain an acceptable signal/noise ratio with our old viscometer but, with the new version (14,15), it is obvious that the maximum value to be used for the [η]*C parameter is around 0.1 in order to avoid concentration effects. This is realistic with regard to a much better signal/noise ratio.

COLUMN CALIBRATION IN IONIC SOLVENTS.

For polyelectrolyte analysis, it is necessary to add salts to water in order to screen out electrical interactions and to get polymers to assume the form of coils. Several solvents: $LiNO_3$ 0.1M, 0.25M, 0.5M, $NaNO_3$ 0.1M, NaCl 0.1M, LiCl 0.1M and Na_2SO_4 0.1M were studied on both column sets and calibration curves were compared to the one obtained in pure water under the same conditions of concentration (C*M=600). The behavior of pullulan and polyethylene oxide standards are represented in Figures 11, 12, 13 and 14 respectively.

Agreement looks good for pullulan standards on Ultrahydrogel columns (Figure 11), except for Na_2SO_4 solvent in which a big increase in elution volumes is observed. However, a discrepancy appears between pure water and other salts on Shodex OH-pak columns (Figure 12), where a small abnormal retention is observed with all the salts, except again for Na_2SO_4 in which the discrepancy is greater.

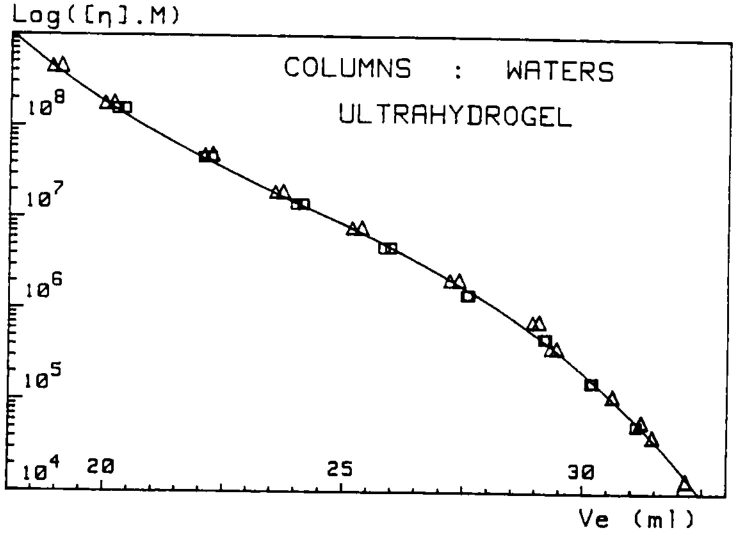

Figure 9. Universal calibration curve at zero concentration and at [η]*C = 0.16. Columns: Ultrahydrogel - Solvent: pure water (□) pullulans - (△) polyethylene oxides.

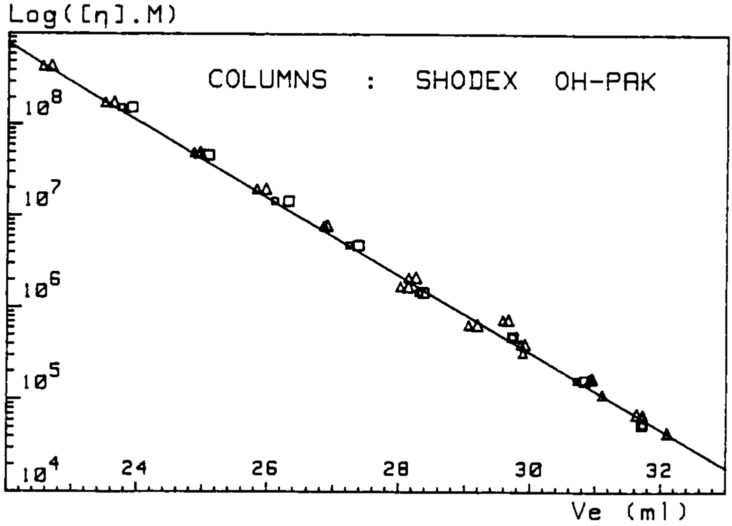

Figure 10. Universal calibration curve at zero concentration and at [η]*C = 0.16. Columns: Shodex OH-pak - Solvent: pure water (□) pullulans - (△) polyethylene oxides.

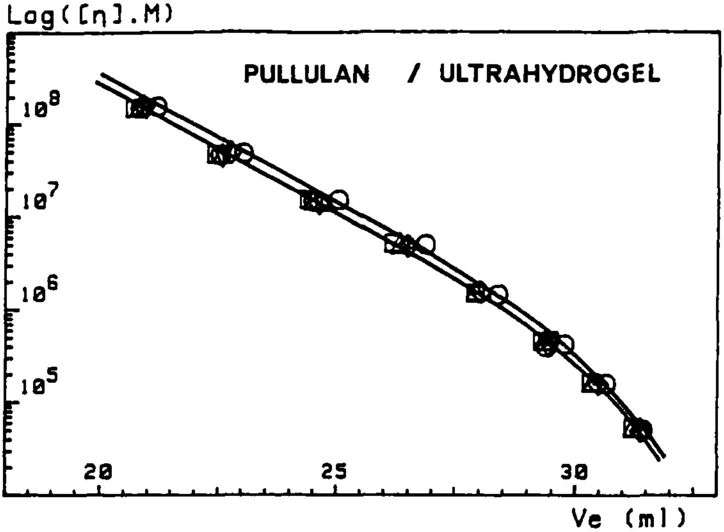

Figure 11. Universal calibration curves of pullulans. Columns: Ultrahydrogel - Solvent used : (□) pure water, (△) $LiNO_3$ 0.1M, (⊘) $LiNO_3$ 0.25M, (▽) $LiNO_3$ 0.5M, (◇) $NaNO_3$ 0.1M, (⊠) NaCl 0.1M, (+) LiCl 0.1M, (○) Na_2SO_4 0.1M.

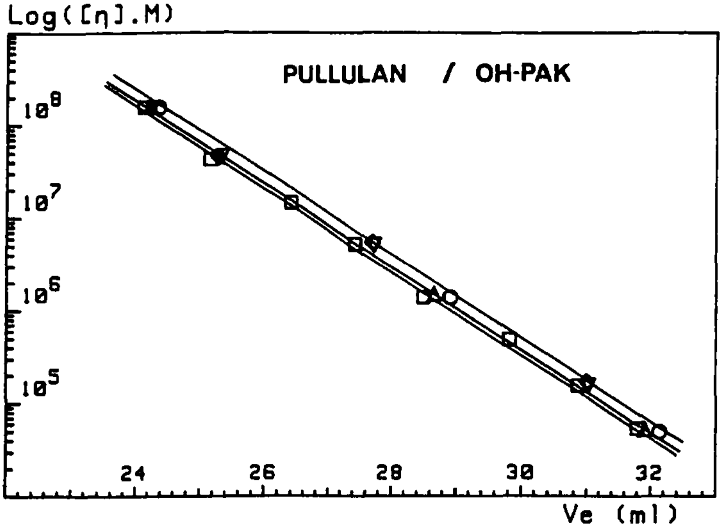

Figure 12. Universal calibration curves of pullulans. Columns: Shodex OH-pak - Solvent used : (□) pure water, (△) $LiNO_3$ 0.1M, (▽) $LiNO_3$ 0.5M, (◇) $NaNO_3$ 0.1M, (○) Na_2SO_4 0.1M.

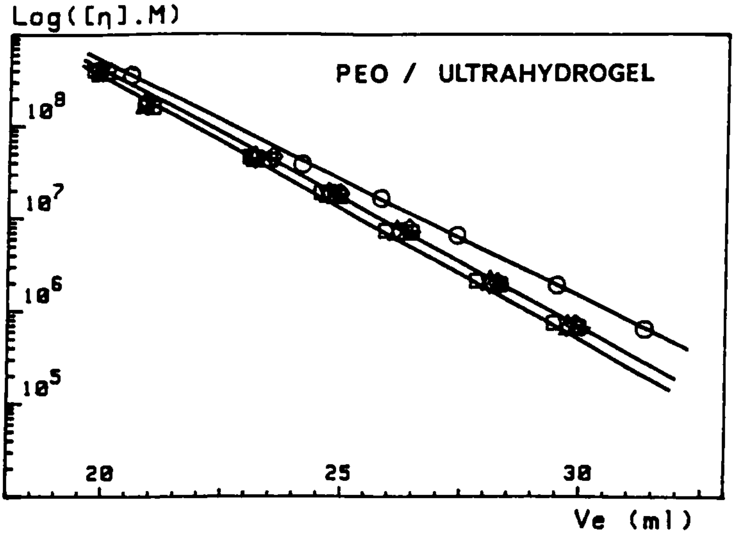

Figure 13. Universal calibration curves of polyethylene oxides. Columns: Ultrahydrogel - Solvent used : (□) pure water, (△) $LiNO_3$ 0.1M, (⊘) $LiNO_3$ 0.25M, (▽) $LiNO_3$ 0.5M, (◇) $NaNO_3$ 0.1M, (⊠) NaCl 0.1M, (+) LiCl 0.1M, (○) Na_2SO_4 0.1M.

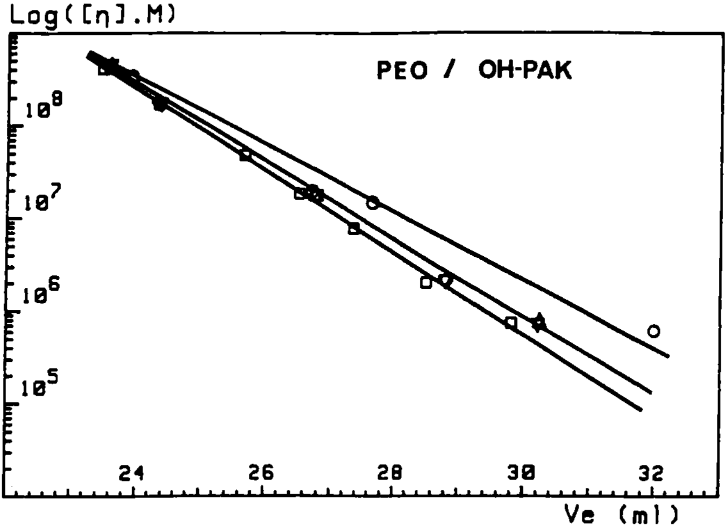

Figure 14. Universal calibration curves of polyethylene oxides. Columns: Shodex OH-pak - Solvent used : (□) pure water, (△) $LiNO_3$ 0.1M, (▽) $LiNO_3$ 0.5M, (◇) $NaNO_3$ 0.1M, (○) Na_2SO_4 0.1M.

For polyethylene oxide standards, the discrepancy looks stronger as well on Ultrahydrogel columns (Figure 13) as on Shodex OH-pak columns (Figure 14). An increase in elution volumes occurs in all salt solutions, mainly in Na_2SO_4 again.

With regard to the phenomenon observed in pure water and, as these results were obtained using the same rule ($C^*M=600$), the question was: **Are the concentration effects responsible of this discrepancy again ?**

Standards were injected again at different concentrations but in only $LiNO_3$ 0.1M solution since no difference has been previously observed between $LiNO_3$, $NaNO_3$, NaCl and LiCl. The corresponding calibration curves, extrapolated to zero concentration, are plotted in Figures 15 and 16 for Ultrahydrogel and OH-pak columns respectively. The dashed curve represents the calibration curve at zero concentration corresponding to pure water. Experimental points at $[\eta]^*C=0$ (the smallest elution volume) and at $[\eta]^*C=0.16$ (the highest elution volume) are represented only.

With Ultrahydrogel columns (Figures 15), agreement looks very good for pullulan standards, whereas abnormal retention occurs in the low molecular weight region for polyethylene oxide standards. The same holds true on Shodex OH-pak columns except that it may exist for pullulans a very small difference between pure water and $LiNO_3$ 0.1M (Figures 16). This result is difficult to confirm despite of a very good checking of flow rate using the viscometer as an on-line flow-meter, since solvent viscosity is not constant when changing from pure water to $LiNO_3$ 0.1M. Nevertheless, the abnormal retention of polyethylene oxide on both column sets seems to be confirmed for molecular weights under 100,000. In every case, a small difference is observed again between $[\eta]^*C=0$ and $[\eta]^*C=0.16$, that confirms the occurence of a weak concentration effect under the $[\eta]^*C=0.16$ condition.

In Na_2SO_4 0.1M solvent, the situation is clearer, neither pullulan nor polyethylene oxide corresponds to the universal calibration curve determined in pure water and represented by a dashed curve, as well on Ultrahydrogel (Figure 17) as on Shodex OH-pak (Figure 18) columns. Moreover, a strong discrepancy arises between both standard sets. This solvent exhibits a particular behavior with abnormal retentions and obviously, must not be used as a chromatographic solvent.

EXAMPLES OF POLYMER CHARACTERIZATION.

In order to carefully check our calibration procedure, we have measured both sets of standards in pure water through light scattering data and viscometric data using calibration achieved with pullulan standards. The comparison between weight average molecular weights is reported in Table I. Obviously, agreement is perfect for pullulans but it looks very good for polyethylene oxides, which means that experimental conditions were perfectly set, avoiding the problem of concentration effects.

Using the same conditions, we have characterized some polymers with different chemical nature, either uncharged (dextran and polyacrylamide) or polyelectrolytes (AM-MSA copolymers: cationic copolymers of acrylamide and N,N,N-trimethyl-aminoethyl-acrylate methyl-

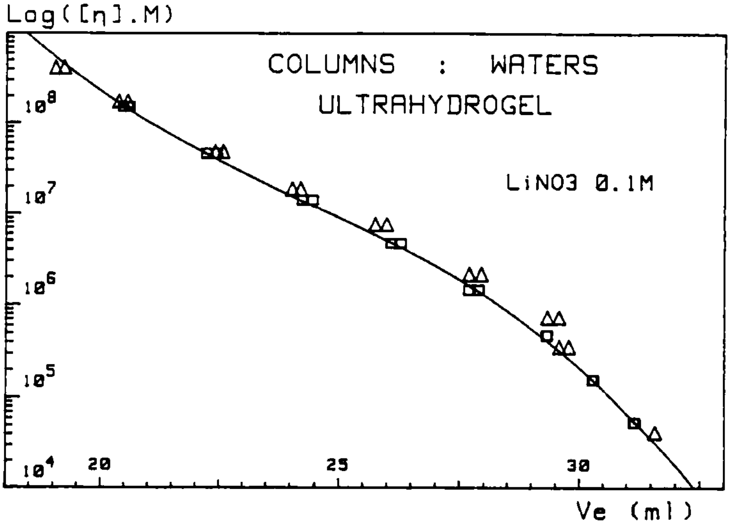

Figure 15. Universal calibration curve at zero concentration and at [η]*C = 0.16. Columns: Ultrahydrogel - Solvent: $LiNO_3$ 0.1M. (□) pullulans - (△) polyethylene oxides.

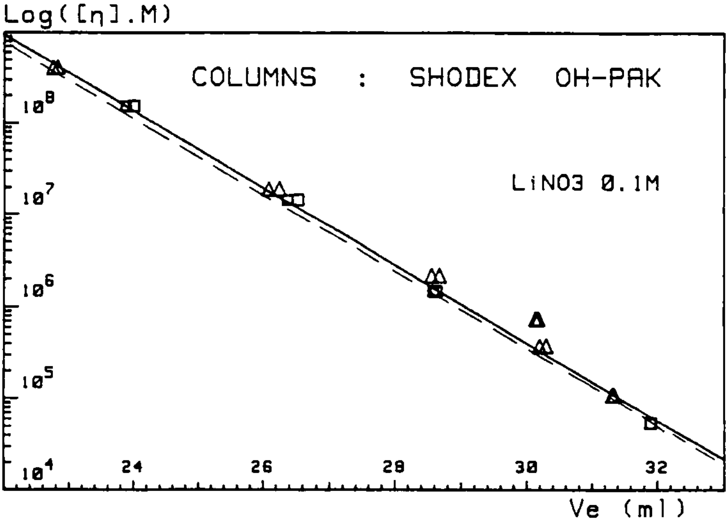

Figure 16. Universal calibration curve at zero concentration and at [η]*C = 0.16. Columns: Shodex OH-pak - Solvent: $LiNO_3$ 0.1M. (□) pullulans - (△) polyethylene oxides.
Dashed curve: universal calibration in pure water.

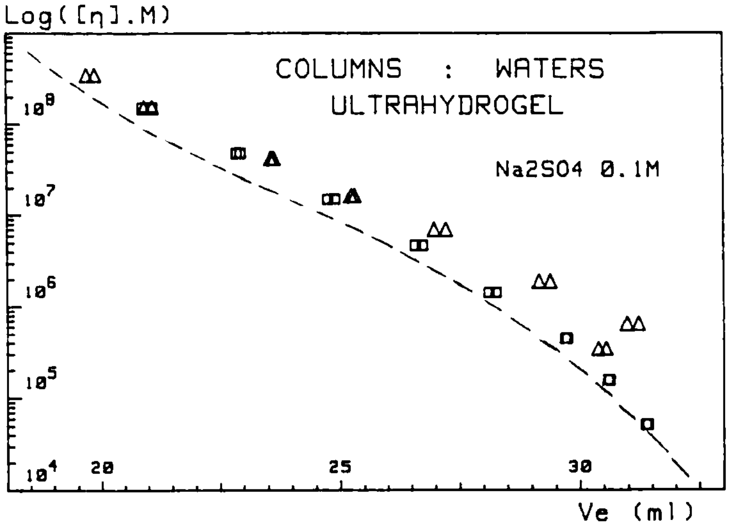

Figure 17. Universal calibration curve at zero concentration and at $[\eta]\cdot C = 0.16$. Columns: Ultrahydrogel - Solvent: Na_2SO_4 0.1M.
(□) pullulans - (△) polyethylene oxides.
Dashed curve: universal calibration in pure water.

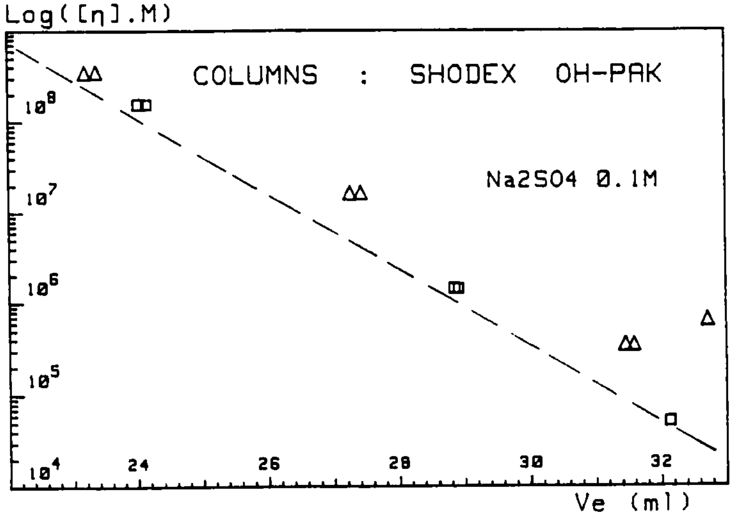

Figure 18. Universal calibration curve at zero concentration and at $[\eta]\cdot C = 0.16$. Columns: Shodex OH-pak - Solvent: Na_2SO_4 0.1M.
(□) pullulans - (△) polyethylene oxides.
Dashed curve: universal calibration in pure water.

POLYETHYLENE OXIDES (Toyo Soda)			**PULLULANS (Showa Denko)**		
TYPE	$\overline{M_w}$ LALLS	$\overline{M_w}$ Univ (*Pu*)	*TYPE*	$\overline{M_w}$ LALLS	$\overline{M_w}$ Univ (*Pu*)
SE 2	21,000	14,000	*PU 5*	7,000	7,000
SE 5	39,000	38,000	*PU 10*	14,000	14,000
SE 8	83,000	91,000	*PU 20*	27,000	26,000
SE 15	142,000	146,000	*PU 50*	53,000	58,000
SE 30	242,000	245,000	*PU 100*	110,000	120,000
SE 70	498,000	491,000	*PU 200*	216,000	219,000
SE 150	851,000	889,000	*PU 400*	427,000	431,000
			PU 800	889,000	937,000

Table I. Weight average molecular weights of standards in pure water. $\overline{M_w}$ LALLS values were determined using LALLS data and $\overline{M_w}$ Univ using viscometric data and universal calibration.

DEXTRANS (DT) and other POLYMERS		
REFERENCE	$\overline{M_w}$ LALLS	$\overline{M_w}$ univ
DT 10,000	10,000	12,000
DT 17,700	14,000	16,000
DT 40,000 A	39,000	54,000
DT 40,000 B	38,000	40,000
DT 40,000	45,000	55,000
DT 66,900	61,000	77,000
DT 83,300	80,000	105,000
DT 170,000	163,000	184,000
DT 234,000	210,000	245,000
DT 500,000	400,000	479,000
DT 500,000	210,000	245,000
DT 2,000,000	2,317,000	1,738,000
Polyacrylamide	128,000	125,000
Copolymer AM-MSA	292,000	267,000

Table II. Weight-average molecular weights of some polymers in pure water and in $LiNO_3$ 0.5M . $\overline{M_w}$ LALLS values were determined using LALLS data and $\overline{M_w}$ Univ using viscometric data and universal calibration.

sulfate). Experiments were run either in pure water or in $LiNO_3$ 0.5M. The results are reported in Table II, where weight-average molecular weights by light scattering and viscometry are compared. For those samples, agreement between both series of values is more than acceptable since discrepancy does not exceed 20%, which demonstrates an excellent running of the GPC system and a perfect behavior of these polymers. But discrepancy can be much higher between light scattering and viscometric data, underlining a poor behavior of samples or a bad control of some GPC parameters, examples will be given in a subsequent paper (23).

CONCLUSION

In conclusion, as molecular weights are determined by two different and independent routes, the triple coupling of GPC with viscometric and light scattering detection, allows for an excellent checking of the GPC analysis. Light scattering detection gives absolute molecular weights and viscometric detection also gives absolute molecular weights but provides an excellent control of solvent flow rate for an accurate reference to the calibration curve. This method is a very useful enhancement for precise characterization of polymers.

However, in order to determine accurate molecular weights, a great attention must be paied to sample concentration and solvent nature, especially in the field of water soluble polymers. It has been shown that the $[\eta]\cdot C$ parameter was well-controlling concentration effects and that its value should not exceed 0.1 in our experimental conditions. Above this value, a significant increase in elution volume is observed leading to an apparent decrease of molecular weight. Under these conditions, a universal calibration can be obtained with pullulan and polyethylene oxide standards on Utrahydrogel and Shodex OH-pak column sets in pure water.

In ionic solvents ($LiNO_3$, $NaNO_3$, NaCl and LiCl 0.1M salts), the situation is less evident. Pullulan standards seem to follow universal calibration whereas a weak discrepancy was observed on Shodex OH-pak columns. Conversely, polyethylene oxide standards exhibit an abnormal retention on both column sets for molecular weights under 100,000. Their use as calibration standards will result in overestimated values, mainly in the low molecular weight region.

For Na_2SO_4 0.1M, the situation is catastrophic since strong abnormal retention occurs in every case, mainly for polyethylene oxides. The use of this solvent is totally prohibited for running a serious GPC analysis of aqueous polymers.

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