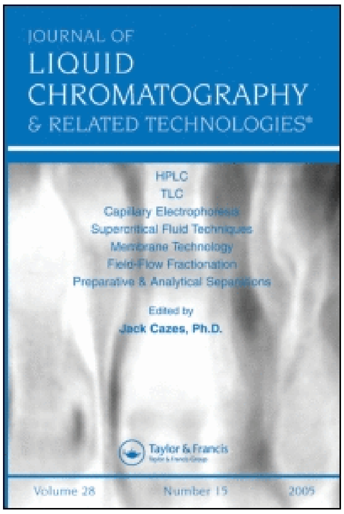

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Characterization of Nonionic Polyacrylamides by Aqueous Size Exclusion Chromatography Using a DRI/LALLSP Detector System

C. J. Kim[a]; A. E. Hamielec[a]; A. Benedek[a]
[a] Department of Chemical Engineering McMaster, University Hamilton, Ontario, Canada

To cite this Article Kim, C. J. , Hamielec, A. E. and Benedek, A.(1982) 'Characterization of Nonionic Polyacrylamides by Aqueous Size Exclusion Chromatography Using a DRI/LALLSP Detector System', Journal of Liquid Chromatography & Related Technologies, 5: 7, 1277 — 1294

To link to this Article: DOI: 10.1080/01483918208067587

URL: http://dx.doi.org/10.1080/01483918208067587

JOURNAL OF LIQUID CHROMATOGRAPHY, 5(7), 1277-1294 (1982)

CHARACTERIZATION OF NONIONIC POLYACRYLAMIDES BY AQUEOUS SIZE EXCLUSION CHROMATOGRAPHY USING A DRI/LALLSP DETECTOR SYSTEM

C.J. Kim, A.E. Hamielec and A. Benedek
Department of Chemical Engineering
McMaster University
Hamilton, Ontario, Canada L8S 4L7

ABSTRACT

Herein is reported an experimental investigation of the molecular weight characterization of nonionic polyacrylamides by aqueous SEC with a DRI/LALLSP detector system. Methodology for the use of the DRI/LALLSP detector responses to determine the molecular weight calibration curve and the peak broadening parameter, σ^2 (variance of a Gaussian instrumental spreading function) over a wide molecular weight range has been developed. The method is based on the use of a broad MWD standard made by blending Polysciences broad MWD standards and a generalized analytical solution of Tung's integral equation for the detector response corrected for peak broadening. Molecular weight averages measured by SEC/DRI/LALLSP are in excellent agreement with those measured offline by LALLSP.

INTRODUCTION

The use of SEC with a LALLSP-based detector system for molecular weight characterization of organic and water-soluble polymers is a recent event.[1,2,3] In fact, methodology for the interpretation of the detector responses is still in the development stage and to date, quantitative methods for the estimation of the molecular weight calibration curve and σ^2 across the chromatogram have been published for one polymer, dextran.[3] A strong interest in the molecular weight characterization of polyacrylamides has recently developed, largely due to the great potential shown by these polymers for enhanced oil recovery via polymer flooding. In fact, the molecular weight distribution of the polymer must be tailored for each reservoir. This, in part, has motivated the present investigation. Polyacrylamides are a good choice for other reasons, the most important of which is the lack of well-characterized standards, whether of narrow or broad MWD. In addition, a suitable packing/mobile phase system has been developed for nonionic polyacrylamides.[4]

THEORY

Tung's integral equation is the starting point for all rigorous methods of correction for peak broadening. For the case of a Gaussian instrumental spreading function, the integral equation takes the form

$$F(v) = \frac{1}{\sqrt{2\pi\,\sigma^2(v)}} \int_0^{\infty} W(y)\,\exp(-(v-y)^2/2\sigma^2(v))\,dy \qquad (1)$$

The use of $\sigma(v)$ rather than $\sigma(y)$ is an approximation which should be valid when the variation of σ with retention volume or molecular size in solutions is not excessive. Molecular weight averages in the detector cell are given by

$$\frac{\overline{M}_K(v,uc)}{M(v)} = \frac{F(v-(K-1)\,D_2(v)\,\sigma^2(v))}{F(v-(K-2)\,D_2(v)\,\sigma^2(v))}\,\exp[(2K-3)(D_2(v)\,\sigma(v))^2/2] \qquad (2)$$

where

$\overline{M}_K(v,uc)$ is the K^{th} molecular weight average of the contents of the detector cell at retention volume v.

$M(v)$ is the molecular weight calibration curve and $D_2(v)$ is the slope of the molecular weight calibration curve which is given by

$$M(y) = D_1(v)\,\exp(-D_2(v)y) \qquad (3)$$

If it is further assumed that the size distribution of polymer solute in the detector cell is Gaussian, it follows that

$$W(v,y) = \frac{F(v)}{\sqrt{2\pi\,\bar{\sigma}^2(v)}}\,\exp(-(y-\bar{y}(v))^2/2\bar{\sigma}^2(v)) \qquad (4)$$

The detector response corrected for peak broadening is then given by[6]

$$W(v) = F(v)(\sigma(v)/\bar{\sigma}(v))\,\exp(-(v-\bar{y}(v))^2/2\bar{\sigma}^2(v)) \qquad (5)$$

$$\bar{y}(v) = v + \frac{1}{D_2(v)} \ln\left(\frac{F(v+D_2(v)\ \sigma^2(v))}{\sqrt{F(v-D_2(v)\ \sigma^2(v))\cdot F(v+D_2(v)\ \sigma^2(v))}}\right) \tag{6}$$

$$\bar{\sigma}^2(v) = \sigma^2(v) + \frac{1}{D_2^2(v)} \ln\left(\frac{F(v-D_2(v)\ \sigma^2(v))\cdot F(v+D_2(v)\ \sigma^2(v))}{F^2(v)}\right) \tag{7}$$

Equation (5) may be applied to either the DRI or the LALLSP detector response. Whole polymer molecular weight averages corrected for peak broadening are given by

$$\bar{M}_K(c) = \int_0^\infty W(v)\ \bar{M}^{K-1}(v)dv / \int_0^\infty W(v)\ \bar{M}^{K-2}(v)dv \tag{8a}$$

$$\bar{M}_K(c) = \int_0^\infty F(v)\ \bar{M}_K^{K-1}(v,uc)dv / \int_0^\infty F(v)\ \bar{M}_K^{K-2}(v,uc)dv \tag{8b}$$

The above equations are employed to develop quantitative methods for determining the molecular weight calibration curve and $\sigma(v)$ across the chromatogram.

EXPERIMENTAL

Instrumentation and operational details for aqueous SEC employed follow.

Columns: 3/8 inch ID X 4-6.5 ft. dry packed with CPG-10 glass packing having pore sizes of 700, 1000 and 3000 Å and particle size, 200/400 mesh.

Mobile phase: 0.20 M Na_2SO_4 with 1 g/25 l Tergitol NPX (Union Carbide Corp.) in deionized distilled water.

Mobile phase flowrate: 1 ml/min.

Detectors: Waters R-401 DRI and Chromatix KMX-6 with angle 6-7° and field stop 0.15.

Inline filter: 0.45 micron Millipore.

Sample loop: 2.0 ml with 0.01-0.1 wt.% polymer solute.

Temperature: ambient.

Polymer standards: nonionic polyacrylamide standards from Polysciences (Warrington, PA) and blends of these standards.

dn/dc: was measured with a Chromatix KMX-16 laser differential refractometer at λ = 632.8 nm and 23°C for nonionic polyacrylamide standards in 0.02 M Na_2SO_4 with 1 g/25 l Tergitol NPX. Values measured were 0.176 (PAM500), 0.168 (PAM1000) and 0.174 (PAM2000).

A_2: the second virial coefficient, A_2, was not used to determine $\overline{M}_W(v,uc)$ as the error involved was neglible at the polymer solute concentrations employed.[3]

RESULTS AND DISCUSSION

Molecular weight calibration curves for single columns containing one pore size are shown in Fig. 1. These calibration

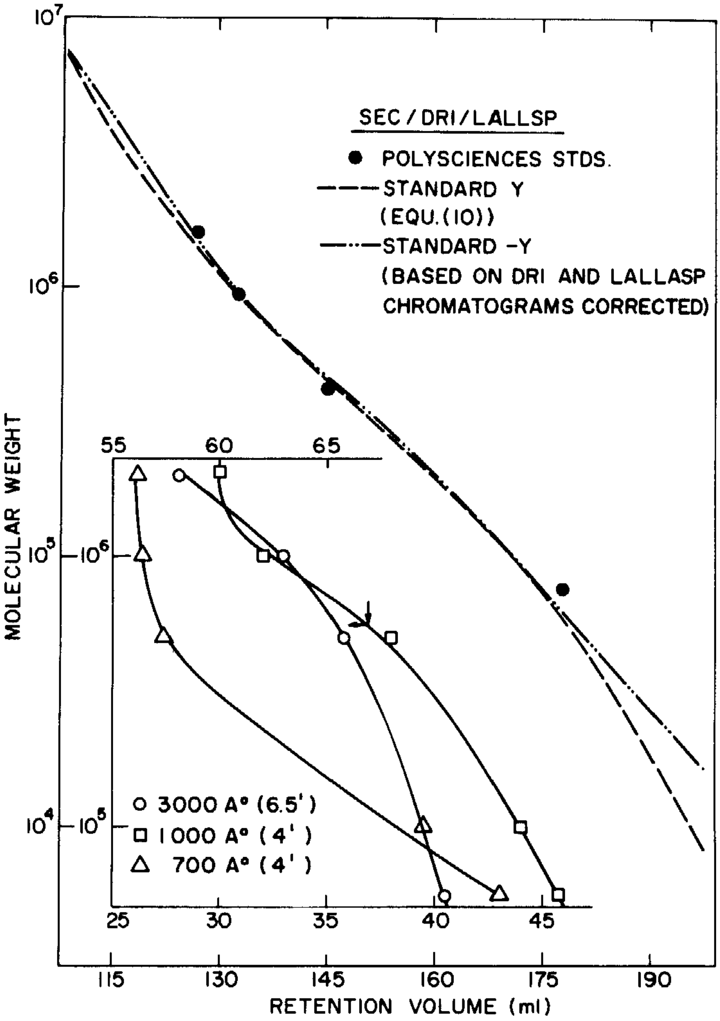

FIGURE 1: Molecular weight calibration curves for single columns and a column combination obtained by different procedures.

curves are approximate as they were obtained using Polysciences broad MWD nonionic polyacrylamide standards and plotting log $\bar{M}_W$ versus peak retention volume. $\bar{M}_N$ values for these standards are not available from the Supplier. These approximate calibration curves are useful in establishing an effective column combination which gives good peak separation over a wide range of retention volumes. It will be later shown that a column set containing 1-4 ft. column with 700 Å pores, 1-4 ft. column with 1000 Å pores and 1-6.5 ft. column with 3000 Å pores gives a molecular weight calibration curve with excellent peak separation and which is almost linear over a wide molecular weight range.

Typical DRI/LALLSP detector responses for PAM2000 (a $2x10^6$ $\bar{M}_W$ Polysciences standard) are shown in Fig. 2. The LALLSP response is very noisy and this is a direct result of the use of a 0.45 µm filter inline. In a previous study with dextrans, a 0.22 µm filter was used and a far less noisy LALLSP response was obtained.[3] To prevent the capture of large polyacrylamide molecules on the inline filter, larger pores are required. The noise level of the LALLSP response was reduced by continually flowing mobile phase at a flowrate of 0.1 ml/min through the columns for long periods of several days to a week before injecting polymer solute. The flowrate is increased to 1.0 ml/min and run for 4 to 6 hours before injection. An acceptable noise level for the LALLSP detector could not be obtained with a 0.65 µm inline filter.

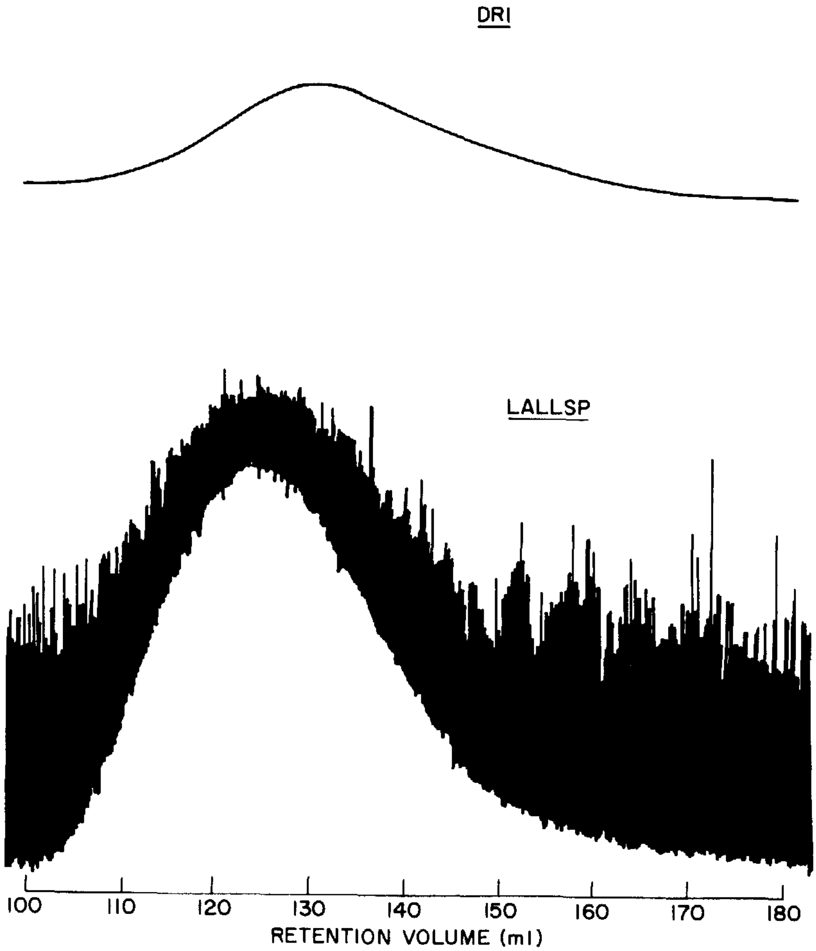

FIGURE 2: DRI/LALLSP detector responses for PAM2000 (a Polysciences nonionic polyacrylamide standard with nominal $\overline{M}_W = 2\times10^6$).

A calculational procedure for finding M(v) and $\sigma(v)$ over a wide range of molecular weights and retention volumes has been reported.[3] This procedure was used here with a blend of Polysciences standards obtained by mixing PAM2000 (42 wt.%), and PAM500 (58 wt.%). The DRI/LALLSP detector responses are shown in Fig. 3. The molecular weight calibration curve, M(v) was obtained by setting $\bar{M}_W(v,uc) = M(v)$ near the peak position of the individual Polysciences standards and this calibration curve is shown in Fig. 1. This calibration curve and the DRI/LALLSP detector responses in Fig. 3 were employed with eqn. (2) to

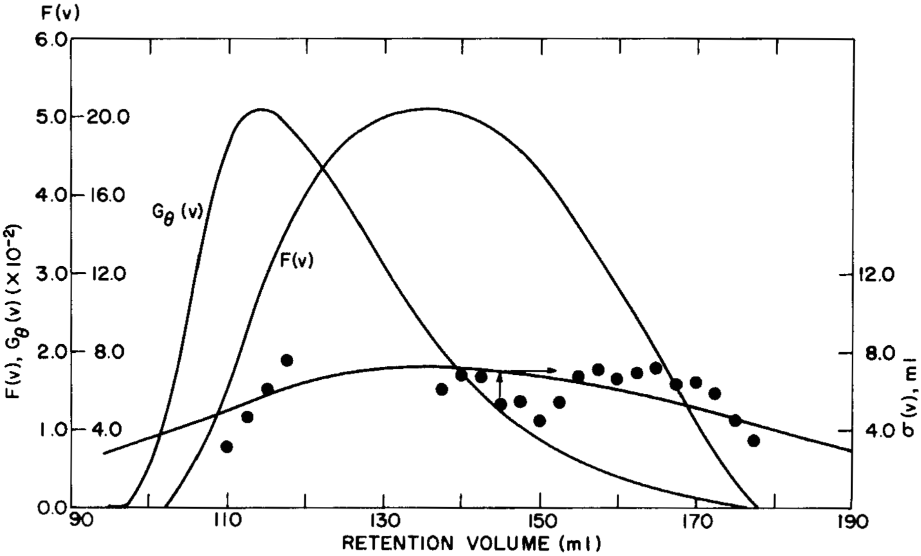

FIGURE 3: DRI/LALLSP detector responses and peak broadening parameter ($\sigma(v)$) for a blend of Polysciences standards (PAM2000 (42 wt.%) and PAM500 (58 wt.%)) designed for $\sigma(v)$ determination.

estimate σ(v) over the retention volume range of the blend. A single-variable search was used to find σ(v) and these results are also shown in Fig. 3. There is considerable scatter in the σ(v) values due to the noisy LALLSP signal; however, the variation of σ(v) with retention volume seems to follow the usual broad bell shape with a relatively small variation with retention volume. A very broad standard, STANDARD-Y, was made by blending PAM200 (13

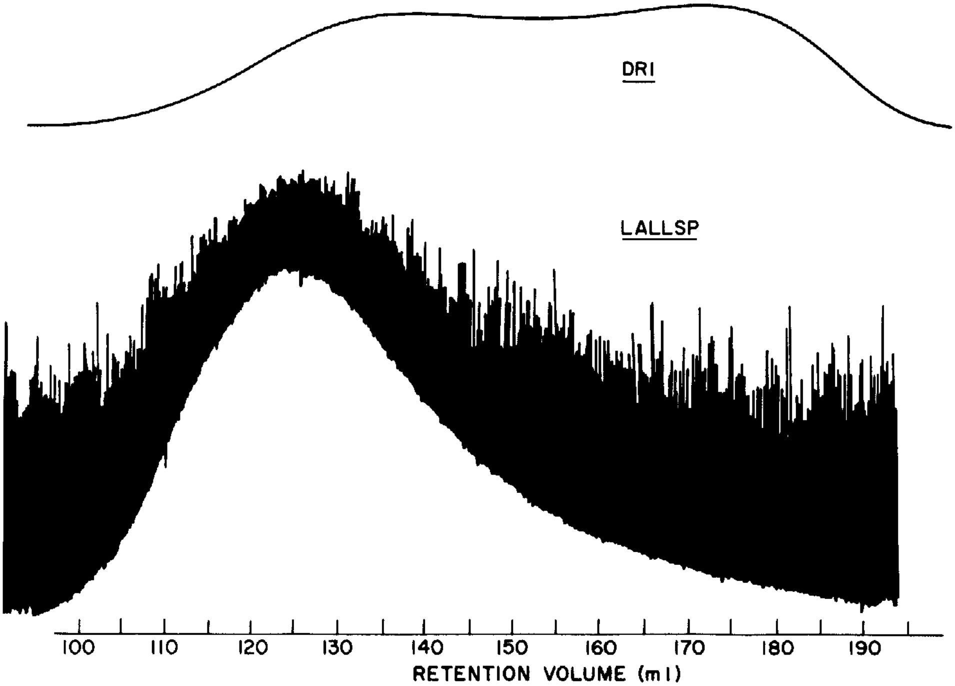

FIGURE 4: DRI/LALLSP detector responses for STANDARD-Y, a blend of Polysciences standards (PAM2000 (13 wt.%), PAM500 (65 wt.%), PAM74 (22 wt.%)) designed for molecular weight calibration curve determination.

wt.%), PAM500 (65 wt.%) and PAM74 (22 wt.%) and was designed to permit the determination of M(v) over a wide range of molecular weights with the DRI/LALLSP detector system. With this standard, it is possible to set $M(v) = \bar{M}_W(v,uc)$ over a wide range of molecular weights and thus find M(v) without the need to correct for peak broadening. The DRI/LALLSP detector response for STANDARD-Y are shown in Fig. 4. To investigate the error involved in M(v) when employing STANDARD-Y and neglecting the peak broadening corrections, a procedure with corrections for peak broadening was used. In particular, the sensitivity of the calculated M(v) to $\sigma(v)$ was investigated. Details of this calculational procedure follow.

It is assumed that in a narrow range of retention volumes $(V_i - V_{i+1})$, the calibration curve is linear. Eqn. (2) may then be written as

$$\ell n\left(\frac{\bar{M}_W(v_i,uc)}{\bar{M}_W(v_{i+1},uc)}\right) = D_2(v_{i+1}-v_i) + \frac{D_2^2}{2}(\sigma^2(v_i)-\sigma^2(v_{i+1}))$$

$$+ \ell n\left(\frac{F(v_i-D_2\sigma^2(v_i)) \cdot F(v_{i+1})}{F(v_{i+1}-D_2\,\sigma^2(v_{i+1})) \cdot F(v_i)}\right) \qquad (9)$$

Given $\sigma(v)$, eqn. (9) is used to solve for $D_2(v)$ and then eqn. (2) is used to find M(v). The results of this computational procedure

TABLE 1

Determination of the Molecular Weight Calibration Curve M(v) Using STANDARD-Y - Sensitivity of M(v) to σ(v)

Retention volume (ml)	$\bar{M}_W(v,uc)/M(v)$				
	σ(v) actual	0.5 σ(v)	0.8 σ(v) (ml)	1.2 σ(v)*	1.5 σ(v)*
118.75	0.734	0.955	0.974	--	--
123.75	0.876	0.798	0.933	--	--
128.75	1.006	1.003	1.004	--	--
133.75	1.065	1.014	1.036	1.118	--
138.75	1.078	1.018	1.048	1.125	--
143.75	1.069	1.017	1.044	1.100	--
148.75	1.065	1.016	1.041	1.095	1.153
153.75	1.052	1.014	1.033	1.073	1.118
158.75	1.046	1.012	1.030	1.065	1.096
163.75	1.056	1.014	1.036	1.078	1.118
168.75	1.052	1.013	1.034	1.074	1.115
173.75	1.078	1.019	1.050	1.115	1.183
178.75	1.100	1.023	1.062	1.141	1.23
183.75	1.113	1.027	1.070	1.166	1.26

* Calculation at low retention volumes were not possible because of excessively large σ(v).

using $\sigma(v)$ values shown in Fig. 3 are summarized as the molecular weight calibration given by eqn. (10).

$$\ln M(v) = 57.52 - 0.789v + 4.93\times10^{-3}v^2 - 1.102\times10^{-5}v^3 \qquad (10)$$

This calibration curve is also shown in Fig. 1. The calculational procedure was repeated using $\sigma(v)$ values smaller and larger than those shown in Fig. 3 to illustrate the sensitivity of the calculated M(v) to $\sigma(v)$. These results are tabulated in Table 1. It is clear that STANDARD-Y can be used to determine M(v) with small error when peak broadening corrections are neglected. This is true for the retention volume range; 128-183 or molecular weight range, 5×10^4 - 2×10^6. Similarly, very broad MWD standards covering higher molecular weights could be made by blending in higher molecular weight polyacrylamides when available.

DRI detector response (raw and corrected for peak broadening) for Polysciences standards PAM2000, PAM1000 and PAM500 are shown in Fig. 5. Corrections are largest at the high molecular weight end of the chromatograms as expected. Corrections for peak broadening were made using eqns. (5,6,7) and the $\sigma(v)$ values in Fig. 3. Detector responses (raw and corrected for peak broadening) for STANDARD-Y obtained using the DRI/LALLSP detector system are shown in Fig. 6. Again, eqns. (5,6,7) and $\sigma(v)$ values shown in Fig. 3 were used to determine W(v). The corrected responses (W(v) chromatograms) were then used to calculate directly the molecular weight calibration curve. It is now

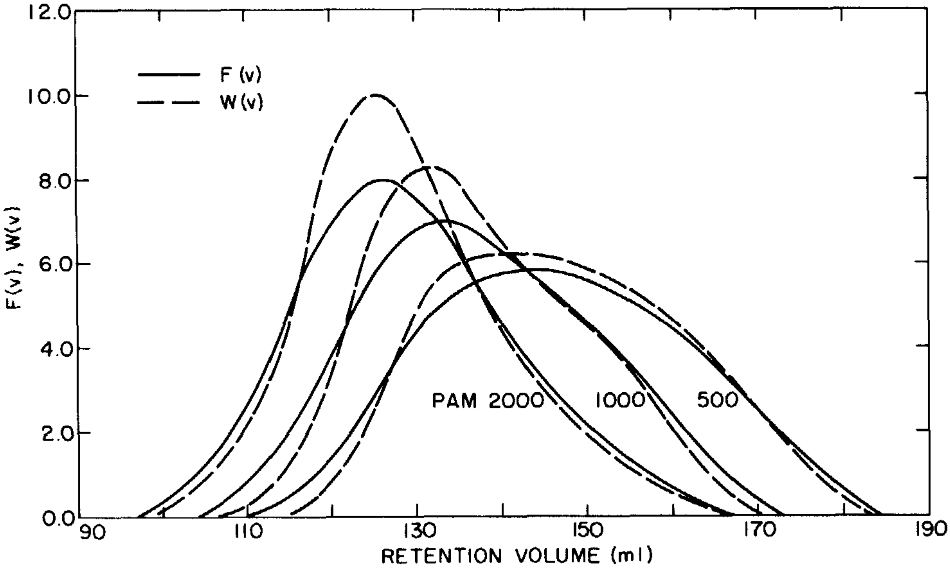

FIGURE 5: DRI detector responses for Polysciences standards (raw (F(v)) and corrected for peak broadening (W(v)) using an analytical solution of Tung's integral equation).

correct to set M(v) = $\bar{M}_W(v)$ at all retention volumes across the detector responses. The M(v) thus obtained is also shown in Fig. 1. The agreement among the molecular weight calibration curves obtained by three different methods is good. In Fig. 7 are shown the $\bar{y}(v)$ and $\bar{\sigma}^2(v)$ values obtained for the STANDARD-Y from the DRI response and also from the LALLSP response. The agreement among these values obtained from responses of very different shape is gratifying and suggests that both responses be used to obtain reliable estimates of $\bar{y}(v)$ and $\bar{\sigma}^2(v)$ over the full molecular weight range of the sample.

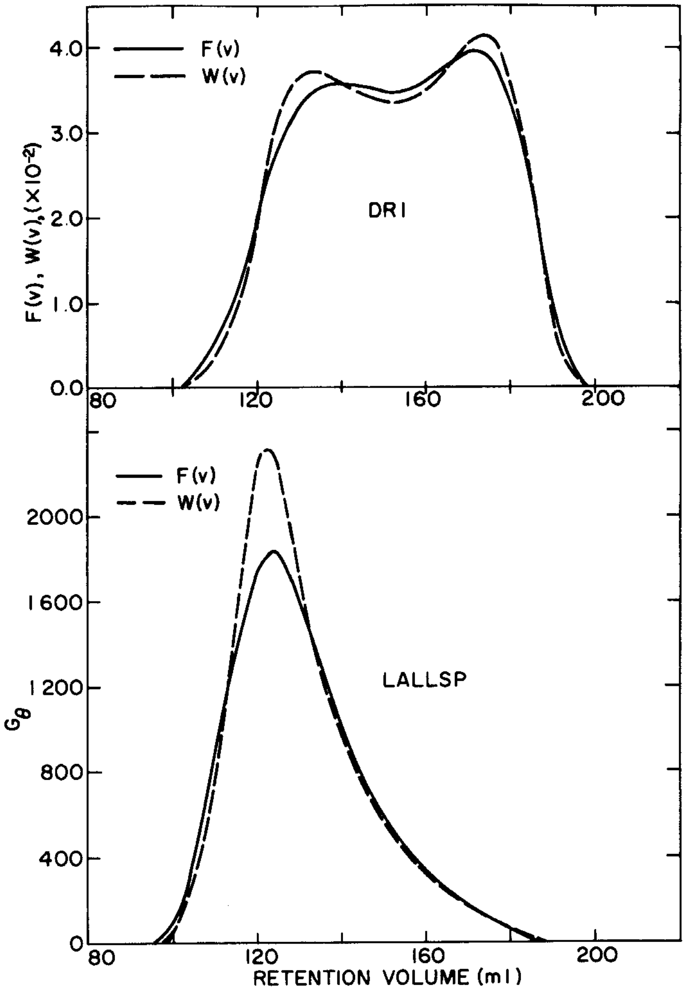

FIGURE 6: DRI/LALLSP detector responses for STANDARD-Y (raw and corrected for peak broadening).

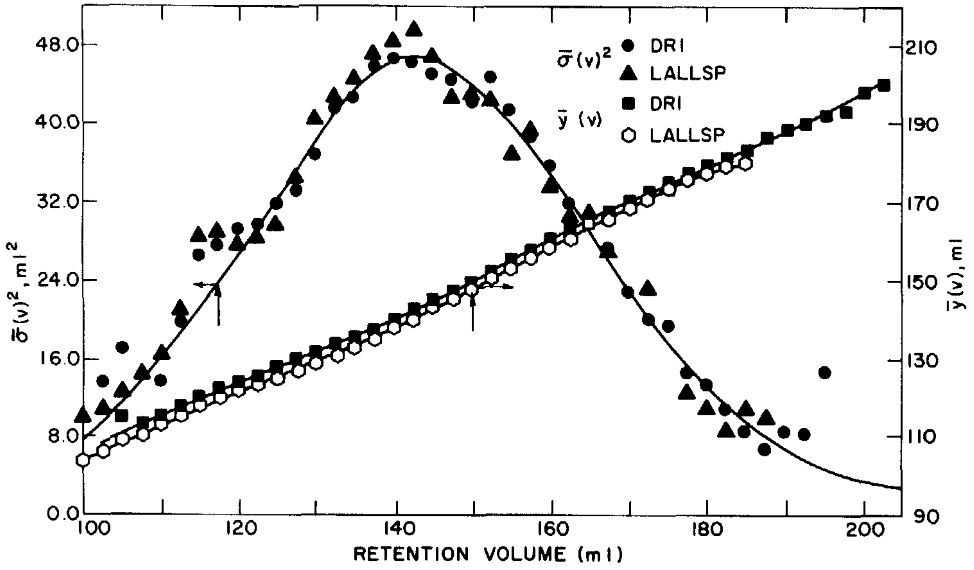

FIGURE 7: Peak broadening parameters for detector cell contents ($\bar{\sigma}^2(v)$ and $\bar{y}(v)$) obtained for both DRI and LALLSP detector responses.

TABLE 2

Whole Polymer $\bar{M}_N(c)$ and $\bar{M}_W(c)$ Values by SEC and $\bar{M}_W$ by LALLSP Offline

Sample	$\bar{M}_W$ (LALLSP) $x10^{-3}$	$\bar{M}_N(c)$ (SEC/DRI/LALLSP)* $x10^{-3}$	$\bar{M}_W(c)$ (SEC/DRI/LALLSP)* $x10^{-3}$	$\bar{M}_N(c)$ (SEC/DRI)** $x10^{-3}$	$\bar{M}_W(c)$ (SEC/DRI)** $x10^{-3}$
PAM2000	2,180	1,198	2200	959	1,880
PAM1000	1,000	608	964	551	988
PAM500	532	283	521	288	571

* Calculated using eqn. (8b).

** Calculated using eqn. (8a).

Finally, whole polymer molecular weight averages $\bar{M}_N(v)$ and $\bar{M}_W(c)$ (averages corrected for peak broadening) measured by SEC using different calculation paths are tabulated in Table 2. The agreement among $\bar{M}_W$ values is within experimental error.

SUMMARY AND RECOMMENDATIONS

Methodology for the interpretation of DRI/LALLSP responses to provide the molecular weight calibration curve and peak broadening parameters (σ^2) over a wide range of molecular weights has been developed and applied successfully to the molecular weight characterization of nonionic polyacrylamides.

The recommended procedure for the molecular weight characterization of nonionic polyacrylamides by aqueous SEC is to use a LALLSP based detector system to determine the molecular weight calibration curve and peak broadening parameters with a specially blended very broad MWD standard, such as STANDARD-Y. The MWD and molecular weight averages for other polyacrylamide samples should then be measured using a mass concentration detector, such as DRI, with application of the analytical solution of Tung's integral equation to provide W(v). In other words, the LALLSP based detector system need only be used for calibration purposes.

REFERENCES

1. Jordan, R.C., J. Liquid Chromatog., 3, 439, 1980.

2. McRury, T.B. and McConnell, M.L., J. Applied Poly. Sci., 24, 651, 1979.

3. Kim, C.J., Hamielec, A.E. and Benedek, A., Characterization of Dextrans by SEC Using a DRI/LALLSP Detector System, J. Liquid Chromatog., in press, 1982.

4. Omorodion, S.N.E., Hamielec, A.E. and J.L. Brash, ACS Symp. Series (ed. T. Provder), No. 138, 267, 1980.

5. Hamielec, A.E., J. Liquid Chromatog., 3, 381, 1980.

6. Hamielec, A.E., Ederer H.J., and Ebert, K.H., J. Liquid Chromatog., 4, 1697, 1981.