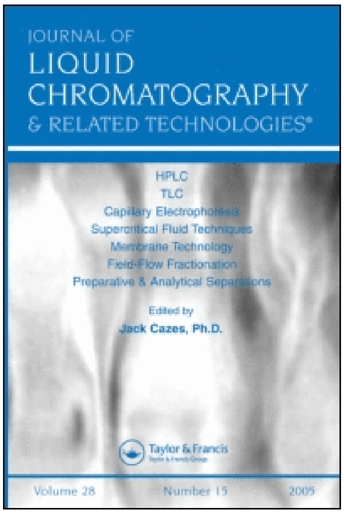

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CHARACTERIZATION OF BRANCHED POLY(VINYL ACETATE) BY GPC AND LOW ANGLE LASER LIGHT SCATTERING PHOTOMETRY

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ABSTRACT

Poly(vinyl acetate), PVAC, synthesized by bulk polymerization over a range of initiator concentrations ([AIBN] = 10^{-5} to 4 x 10^{-3} g-mole/l), temperatures (50°C, 60°C, 70°C, and 80°C) and conversion levels (3 to > 90%) were characterized using low angle laser light scattering (LALLS) photometry to measure $\bar{M}_w$ of the whole polymers. A number of these samples were characterized using GPC with a differential refractive index (DRI) and LALLS detector to measure the molecular weight distribution (weight fraction versus M_w). $\bar{M}_w$ for PVAC samples synthesized at suitably low initiator levels at various conversions were found to agree with classical light scattering measurements after Graessley.

An electronic device and a technique which optimizes the sensitivity and the signal-to-noise ratio of the LALLS photometer throughout the molecular weight distribution (MWD) of the GPC chromatogram were devised. These considerably simplify the operation of the LALLS for both offline and online operation with GPC.

Most importantly it was unambiguously shown that the commonly used universal calibration parameter (UCP) with GPC, $[\eta]M_w$, is incorrect for polymers with molecules having the same hydrodynamic volume but different molecular weights, i.e., those with only chain branching (LCB), copolymers with compositional drift, and polymer blends. The correct UCP was found to

be $[\eta]M_n$, where M_n is the number average molecular weight. This UCP provides a sound basis for the characterization of complex polymers by GPC with a viscometer detector and for the characterization of branched polymers by GPC with a DRI detector using an indirect method which involves a knowledge of whole polymer intrinsic viscosity.

INTRODUCTION

In previous publications (1-3) it was demonstrated that LALLS coupled to a GPC chromatograph gave self consistent data on the molecular weight distribution of linear polymers. In this work we took advantage of the unique characteristics of LALLS and GPC to study branched polymers. We were particularly interested in investigating the controversy regarding the applicability of the universal calibration concept to polymers with long chain branching (LCB), i.e., polyethylene (4-5) and PVAC. We also wanted to establish whether LALLS offline and online with GPC provides useful information on the molecular architecture of polymers with long chain branching.

PVAC was selected as the model polymer to study for the following reasons: (a) It is a commercially important polymer and its synthesis mechanism resembles that of low density polyethylene which is also an important material. (b) PVAC is soluble in a wide variety of solvents, particularly in THF which is the most widely used room-temperature solvent for GPC. (c) The PVAC synthesis mechanism has been comprehensively investigated (6).

This work is reported in two parts. In Part 1 we discuss the offline LALLS measurement of the weight average molecular weight, $\overline{M}_w$, of the whole polymer over a wide range of $\overline{M}_w$ and conversions. This permits the measurement of the second virial coefficients, A_2, as a function of $\overline{M}_w$, information which is essential for the online LALLS/GPC measurement. These offline measurements also permit comparison with $\overline{M}_w$'s determined in the earlier work of Graessley (6) and values predicted by kinetic theory. Part 2 concerns the online (LALLS coupled with GPC) measurement of M_w as a function of retention volume over the GPC chromatogram. This allows investigation of the M_w-hydrodynamic volume relationship, and the validity of the universal calibration concept for polymers with LCB. The online coupling of the LALLS to the GPC chromatograph also provides an accurate measurement of the molecular weight distribution (weight fraction versus M_w) for branched PVAC.

EXPERIMENTAL

A. PVAC Synthesis

The PVAC samples were prepared by bulk polymerization using various levels of AIBN initiator, conversions and temperatures (8). The initiator concentration was varied from 10^{-5} to 4×10^{-3} g mole/l and the polymerization was carried from 2.3% to almost 100% conversion. Polymerization temperatures investigated were 50, 60, 70 and 80°C.

B. ΔN/ΔC Measurements

The refractive index increments of PVAC were measured in THF (distilled in glass grade by Burdick and Jackson) and toluene (cp grade) at 24°C using a Brice Phoenix differential refractometer. The light source was a mercury lamp with a very narrow-pass band filter at 6100°A wavelength. The concentration range used varied from 2 g/l to 10 g/l. The ΔN/ΔC value obtained for PVAC in THF was 4.80×10^{-2} ml/g and for PVAC in toluene was -1.83×10^{-2} ml/g. The ΔN/ΔC in toluene was measured to permit comparison of our measured $\bar{M}_w$'s with those for the same PVAC samples measured separately in toluene with LALLS.

C. Offline LALLS Photometry

The details of the design of the LALLS photometer have already been discussed elsewhere (1,2). However, the procedure for determining the Rayleigh factor R_θ of the solvents and the PVAC solution is briefly described here.

Stock solutions of accurately weighed PVAC samples were prepared in 25 ml volumetric flasks with THF. Three other concentrations were prepared by diluting the stock solution by 1/2, 1/5 and 1/10. In the case of the very high molecular weight samples, dilutions of 1/20 were made in lieu of the 1/2 stock solution concentration.

The R_θ's of the solvent and solutions were obtained using the following procedure: (1) The solvent of the solution was injected into the flowthrough sample cell using a syringe equipped with a filter cartridge of 0.2 µm porosity Teflon filter (Millipore FGLP01300). After ascertaining that the injected solution had displaced the previous sample in the cell, the annulus and the field stop were set at 6.5° (6-7 setting) and 0.2 mm, respectively. (2) The gain of the photomultiplier was adjusted to give a recorder reading of about 100%. The actual recorder reading is recorded as G_θ. (3) The calibrated neutral density filters (optical attenuators) 1, 2, and 3 are interposed in the laser beam. (4) The annulus and the field stop are set to 0° and 1.5 mm, respectively. (5) A combination of the optical attenuators 1 to 3 are then pulled out of the beam such that a maximum response of the recorder is obtained. The recorder reading and the set of attenuators in the beam are recorded. This data along with the optical constants of the photometer gives G_o. (6) G_o is calculated in this manner:

$$G_o = (\text{recorder reading})\,|D(\sigma'\ell')^{-1}$$

where D is the optical attenuation and the $(\sigma'\ell')^{-1}$ is the instrumental constant which is supplied by the manfacture (Chromatix). (7) The Rayleigh factor is calculated as

$$R_\theta = G_\theta/G_o\ .$$

The molecular weight and the second virial coefficient, A_2, can be obtained by plotting the value $\frac{KC}{\bar{R}_\theta}$ against the concentration. K is the polymer constant defined as:

$$K = \frac{2\pi^2 N^2 (\Delta N/\Delta C)^2 (1+\cos^2\theta)}{\lambda^4 \; N_{avg.}} \tag{1}$$

and $\bar{R}_\theta$ is the excess Rayleigh factor defined as

$$\bar{R}_\theta = R_\theta^{solution} - R_\theta^{solvent}$$

and C is the concentration. Usually, the plot of $\frac{KC}{\bar{R}_\theta}$ versus C is a straight line with an interpret

$$\left(\frac{KC}{\bar{R}_\theta}\right)_{C\to 0} = \frac{1}{\bar{M}_w} \tag{2}$$

and the slope gives A_2.

D. Online GPC/LALLS Photometry

The GPC chromatograph used in this work was not a commercial chromatograph, but was built from components as illustrated in Fig. 1. The inlet of the LALLS sample cell (with an integrated filter) was connected to the outlet of a system of 5 high-speed (Microstyrogel) columns having permeability limits ranging from 10^3 Å to 5 x 10^6 Å (Waters' Associate designation) with a 1/16" Teflon tubing 24 inches long, having an inside diameter of 0.01". The outlet of the LALLS sample cell was connected directly to a Waters Associate R401 differential refractometer by a 12" Teflon tubing with the above specification. The LALLS filter and sample cell had a total volume of only 10 μℓ and the total mixing volume added to the system by the LALLS was only 25 μℓ.

The filter used to provide a good clean signal for the LALLS was a 0.45 μ silver filter (Selas) in series with a 0.25 μ Teflon filter (Millipore). This system provided a relatively particle-free solution in the LALLS scattering

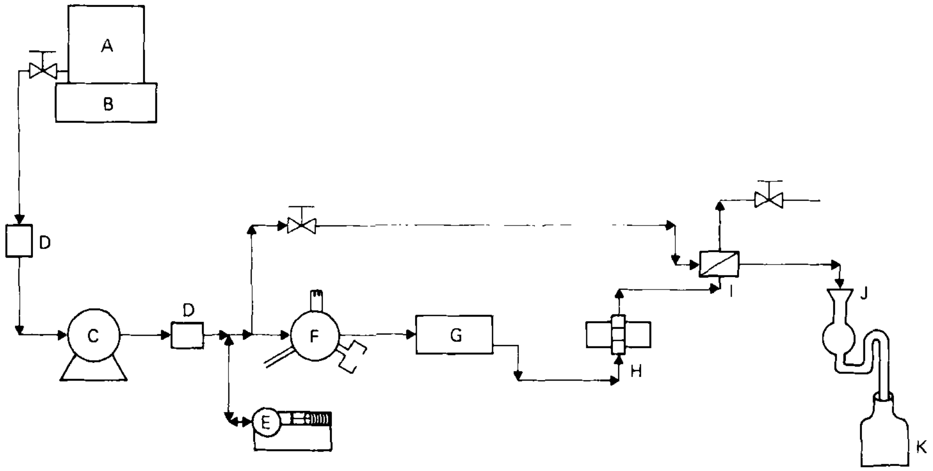

Fig. 1 Schematics of the GPC/LALLS system (a) solvent reservoir, (b) magnetic stirer, (c) syringe metering pump, (d) filter, (e) pulse damping system, (f) sample injection valve, (g) fractionating column, (h) LALLS photometer, (i) DRI, (j) siphon volume counter, (k) waste solvent.

volume without significant removal of the high molecular weight fraction of the sample. There was no significant pressure drop build up in the filter during injection of the samples.

To determine the concentration of the GPC effluent from the DRI equipped chromatograph, the following relationships are derived:

Let v = retention volume in ml

$H(v)$ = DRI response

If we assume that $H(v)$ is independent of molecular weight of the effluent then

$$H(v) = k\,C(v) \tag{3}$$

where C(v) is the polymer concentration of a particular retention volume. The total weight (W_T) of the polymer injected into the GPC is related to the chromatogram total area (A_T),

$$W_T = \sum_{V_o}^{V_f} C(v)\Delta V = \frac{1}{k}\sum_{V_o}^{V_f} H(v)\Delta V = \frac{A_T}{k} \tag{4}$$

therefore

$$C(v) = \frac{W_T}{A_t} H(v) \tag{5}$$

In terms of the DRI chromatogram height and area, and the instrumental constants, (5) can be rewritten as:

$$C(x) = \frac{W_T R_s}{A_T' Q} y(x) \tag{6}$$

where y(x) and A_T' are the heights of the chromatogram in cm at any x (the abscissca of the chromatogram) and the total area in cm^2 of the chromatogram, respectively. R_s and Q are the recorder chart speed in cm/sec and flow rate in cm^3/sec, respectively. The W_T is calculated from the concentration of the polymer solution and the volume of a calibrated sample injection loop (1.008 ml). Q is calculated from the syphon volume and the syphon dump frequency.

The corresponding Rayleigh factor R_{θ_i} is determined from the LALLS signal for the fraction of interest. The molecular weight, M_{w_i} of the fraction is computed from the equation

$$\frac{1}{M_{w_i}} = \frac{KC_i}{R_{\theta_i}} - A_2 C_i \tag{7}$$

where K and A_2 are the polymer constant and the second virial coefficient, respectively. Further details of the experimental procedure and description of the LALLS can be found in References 1-3.

RESULTS AND DISCUSSION

A. Offline LALLS

Figure 2 shows plots of $KC/\overline{R}_\theta$ versus concentration for the Series-4 PVAC samples. It is apparent that the plots show upward curvature particularly at concentrations greater than 2 gram/l. This suggests that the 3rd virial coefficient has a significant contribution to the $KC/\overline{R}_\theta$ dependence on concentration. For samples which exhibit a strong 3rd virial coefficient, a linear relationship can often be obtained by plotting the $\sqrt{KC/\overline{R}_\theta}$ versus the concentration. Figure 3 shows this linear relationship for the Series-4 PVAC samples shown in Fig. 2. It is apparent that the value of $(KC/\overline{R}_\theta)_{c\to 0}$ can be more precisely obtained from the linear plot of Fig. 3 than from Fig. 2. However, the $\overline{M}_w$'s calculated from Figs. 2 and 3 were found to agree within 10%, mainly because the curva-

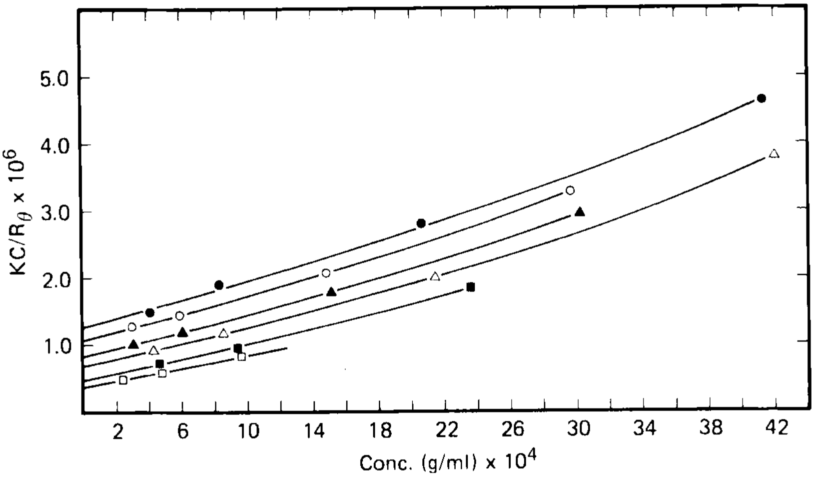

Fig. 2 Rayleigh ratio versus concentration plots for PVAC synthesized at 60°C and 2 x 10^{-3} g-mole/l AIBN concentration at percent conversion of ● - 21.25, ○ - 37.40, ▲ - 54.46, △ - 64.68, ■ - 82.31 and □ - 92.60.

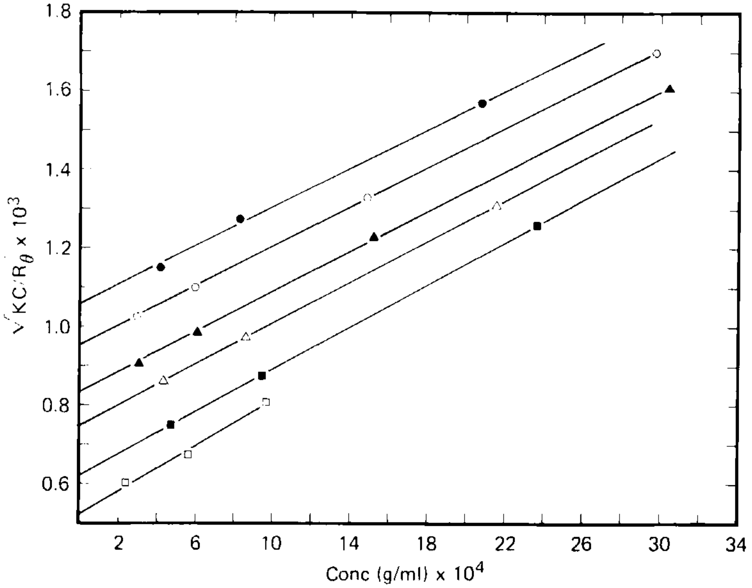

Fig. 3 The square root of the Rayleigh ratio versus the concentration plots for PVAC samples shown in Fig. 2. The same symbols are used to represent various levels of conversion as in Fig. 2.

ture of the plots in Fig. 2 are not severe, permitting reasonably accurate extrapolation to $(KC/\bar{R}_\theta)_{c\to 0}$.

The interlaboratory reproducibility of $\bar{M}_w$ data for the LALLS was tested with PVAC samples B-7 and C-9. Dr. McRury obtained $\bar{M}_w$'s of 3.4×10^6 for the B-7 and 2.0×10^6 for C-9, which compare reasonably well with the $\bar{M}_w$'s of 2.9×10^6 for the B-7 and 2.2×10^6 for the C-9 obtained in this study.

The second virial coefficients for PVAC samples synthesized at 80°C and 60°C with low and comparable level of initiator concentrations were measured and plotted against the molecular weight as shown in Fig. 4. For linear polymers such as polystyrene and poly(methyl methacrylate), the A_2 have been shown

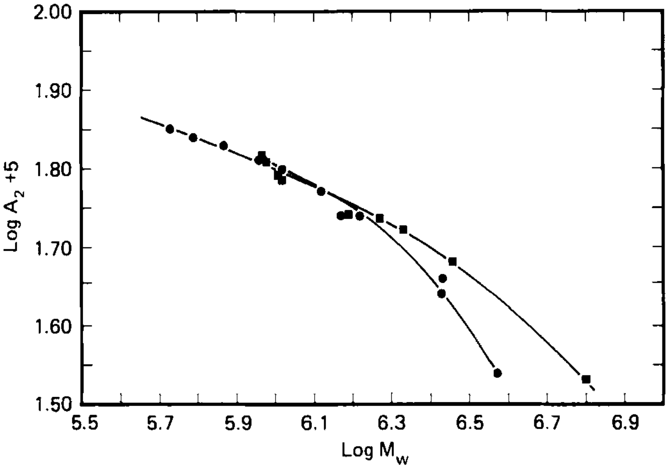

Fig. 4 Log-log plots of the second virial coefficient A_2 versus the weight average molecular weight, M_w, for PVAC synthesized at ● - 80°C and ■ - 60°C with [AIBN] = 10^{-5} g-mole/l.

(1,2) to follow a linear relationship with $\bar{M}_w$ in log-log scale. It is interesting to note that, in the lower $\bar{M}_w$ and lower conversion range, the log A_2 versus log $\bar{M}_w$ appears to be linear. However, there is a rapid decrease in A_2 for samples at higher conversions and therefore higher branching frequency and molecular weight. Furthermore, the PVAC samples which were prepared at 80°C exhibit a more rapid decrease in A_2 with increasing $\bar{M}_w$. Since A_2 is proportional to the excluded volume (7) and since the excluded volume decreases with increasing branching frequency at constant $\bar{M}_w$, we can infer from Fig. 4 that the PVAC polymers prepared at 80°C have a higher branching frequency but shorter branches than the PVAC polymers prepared at 60°C of comparable $\bar{M}_w$.

As mentioned in the Introduction, one of the reasons for our interest in PVAC is that its polymerization kinetics are well understood and therefore comparison between $\overline{M}_w$ data with theory is possible. Figure 5 shows the dependence of the $\overline{M}_w$, the number average molecular weight, $\overline{M}_N$, (from Illahie (8) and Thomas (9)) and the average number of branches per molecule, B_N (from theory), on the conversion at 80°C and 10^{-4} g-mole/l [AIBN] synthesis conditions. It is clear that the $\overline{M}_w$ and $\overline{M}_N$ predicted by theory as developed by Graessley (6) agrees reasonably well with the experimental $\overline{M}_w$ and $\overline{M}_N$. The values of the kinetic parameters Cm, Cp and K were obtained by fitting measured $\overline{M}_w$ at various conversions.

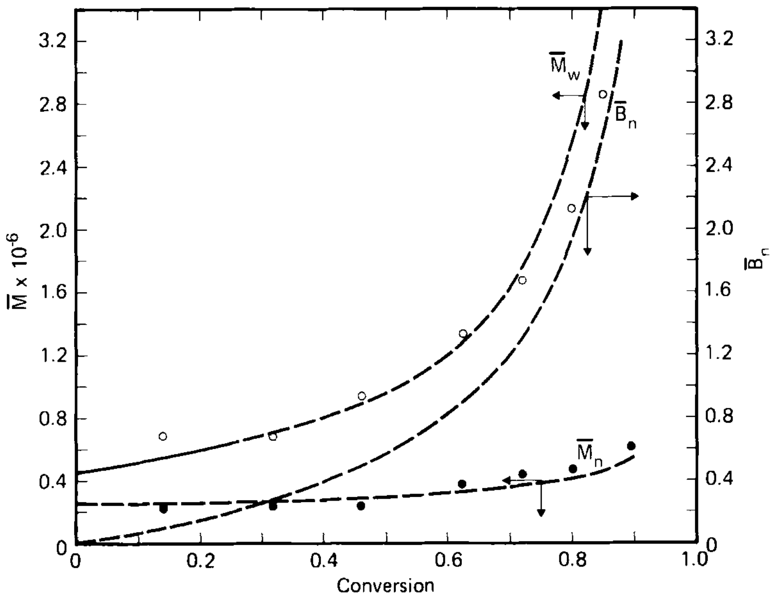

Fig. 5 A plot of the M_w, M_N (8 and 9), and B_n versus percent conversion for PVAC samples synthesized at 80°C and [AIBN] = 10^{-4} g-mole/l. — — — theory (CM = 3.5×10^{-4}, CP = 2.5×10^{-4} and K = 0.56).

Figure 6 shows the effect of initiator concentration on the variation of $\bar{M}_w$ with conversion at 80°C synthesis temperature. At lower conversions, the effect of the initiator concentration appears to be minimal. However, at conversion levels greater than 70%, the molecular weight of the PVAC prepared with the higher initiator concentration appears to have significantly lower $\bar{M}_w$ than the polymer prepared of the lower concentration of AIBN.

Figure 7 shows the dependence of $\bar{M}_w$ on conversion and on AIBN concentration at 60°C synthesis temperature. Also shown is a comparison among theory, Graessley's data (6) and our data. Increasing the initiator concentration clearly

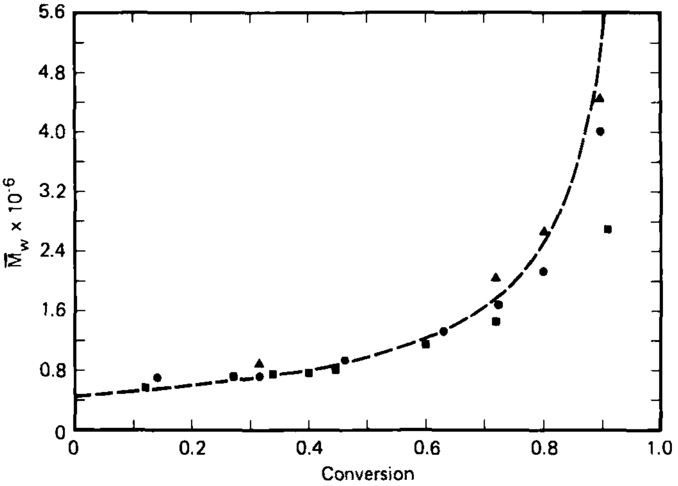

Fig. 6 A plot of the M_w versus percent conversion for PVAC synthesized at 80°C and two different levels of initiator concentration. ● - [AIBN] = 10^{-4} g-mole/l, LALLS offline data, ▲ - [AIBN] = 10^{-4} g-mole, LALLS/GPC online data, ■ = 2 x 10^{-4} g-mole/l, LALLS offline data. — — —theory (CM = 3.5 x 10^{-4}, 2.5 x 10^{-4}, K = 0.56).

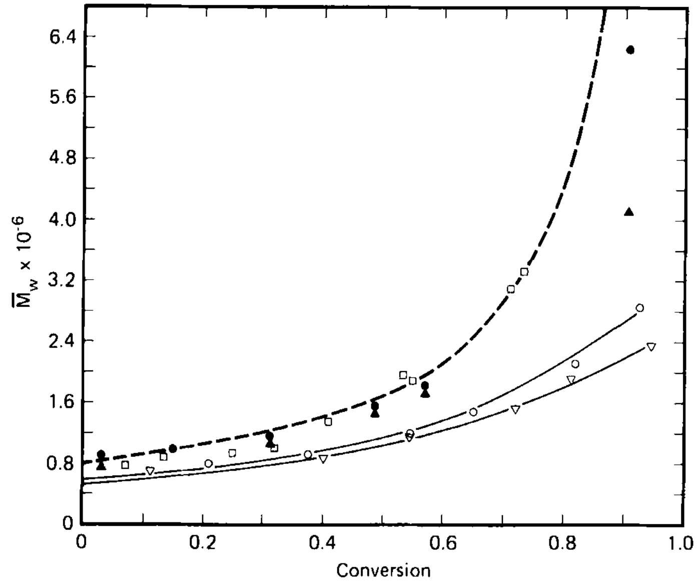

Fig. 7 A plot of the M_w versus percent conversion for PVAC synthesized at 60°C and three levels of initiator concentrations. ● - [AIBN] = 10^{-5} g-mole/l, LALLS offline, ▲ - [AIBN] = 10^{-5} g-mole/l, LALLS/GPC online data, ○ - [AIBN] = 2 x 10^{-3} g-mole/l, LALLS offline data, △ - [AIBN] - 4 x 10^{-3} g-mole/l, LALLS offline data, □ - Graessley's (6) data — — — theory (CM = 2 x 10^{-4}, CP = 1.5 x 10^{-4}, K = 0.56).

depresses the molecular weight. This effect is probably due to the decrease in the main chain length and the LCB length. Thus, at higher conversion for the same branching per unit main chain length, the molecular weight of the PVAC synthesized at higher AIBN concentration will be lower than those prepared with the lower initiator concentration.

Although the agreement among theory, Graessley's data and our data (initiator concentration ~ 10^{-5}) at the lower concentration ([AIBN] = 10^{-5} g mole/l) level is reasonably good, there is substantial deviation of the experimental data from the theory above 80% conversion. There are at least three possible explanations for these observations: (1) the theory may not be valid at higher conversion; (2) the accuracy of the $\bar{M}_w$ measurements may degrade, because the homodyne beating (which can resemble scattering from dust particles) of extremely high molecular weight polymer causes difficulty in accurately determining the time average light scattering intensity of the solution; (3) at high conversion, the small error in the percent conversion measurement results in very large changes in $\bar{M}_w$. Of the three explanations, (1) and (3) are the most probable because LALLS data of $\bar{M}_w > 7 \times 10^6$ have been measured reliably (2).

Further comparison between the experimental data and theory is obtained from the dependence of $\bar{M}_w$ versus conversion at 70°C synthesis temperature shown in Fig. 8. The kinetic constants Cm and Cp were obtained by extrapolating the 60°C and 80°C data and using the Arrhenius equation. As in Fig. 7, the agreement between theory and experimental data is very good at low initiator concentration (Graessley's data (6)) and conversion. The polymers prepared with higher ([AIBN] = 10^{-3} g-mole/l) initiator concentration show a substantually lower $\bar{M}_w$ than Graessley's data (6) (prepared at a much lower [AIBN] ~ 10^{-5} g-mole/l) and $\bar{M}_w$'s predicted by theory.

B. Online GPC/LALLS

Typical chromatograms of a high conversion PVAC sample using both the DRI and LALLS detectors are shown in Fig. 9. It is immediately apparent that the peaks of the DRI and the LALLS for the broad distribution samples are not in coincidence despite the very small (~ 25 μℓ) mixing volume between the LALLS and the DRI sample cells. The LALLS chromatogram is offset towards the lower retention volume or the higher molecular weight portion of the chromatogram relative to the

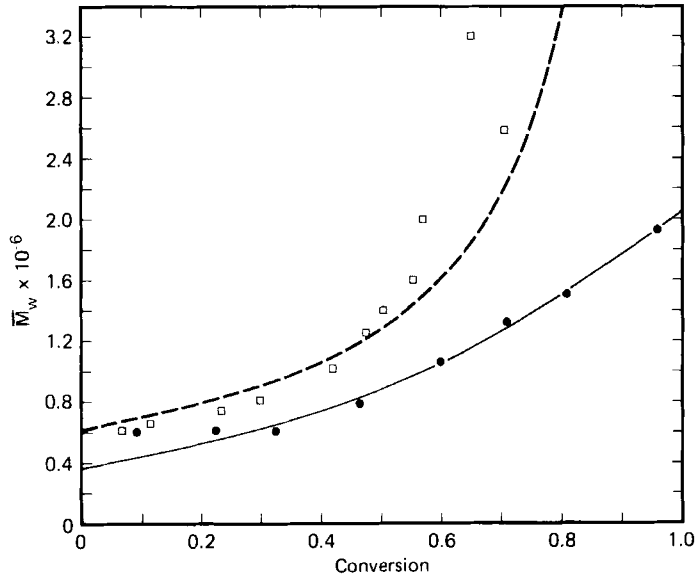

Fig. 8 A plot of the M_w versus percent conversion for PVAC synthesized at 70°C and [AIBN] = 10^{-3} g-mole/l. ● - LALLS offline data, □ - Graessley's (6) data, — — — theory (CM = 2.66×10^{-4}, CP = 1.96×10^{-4}, K = 0.98).

DRI response. The stronger response of the LALLS detector to the higher end of the MWD is as expected, for the intensity of the scattered light is proportional to the product of the mass concentration and the molecular weight of the sample (Eq. 4).

The difference in the sensitivity of the DRI and the LALLS detectors at both ends of the chromatograms (shaded area of Fig. 9) poses a problem for calculating the molecular weight of the sample at both ends of the chromatogram and the whole polymer average molecular weights precisely, because the magnitude of both signals must be accurately known to calculate the M_w of any fraction of the chromatogram. To solve

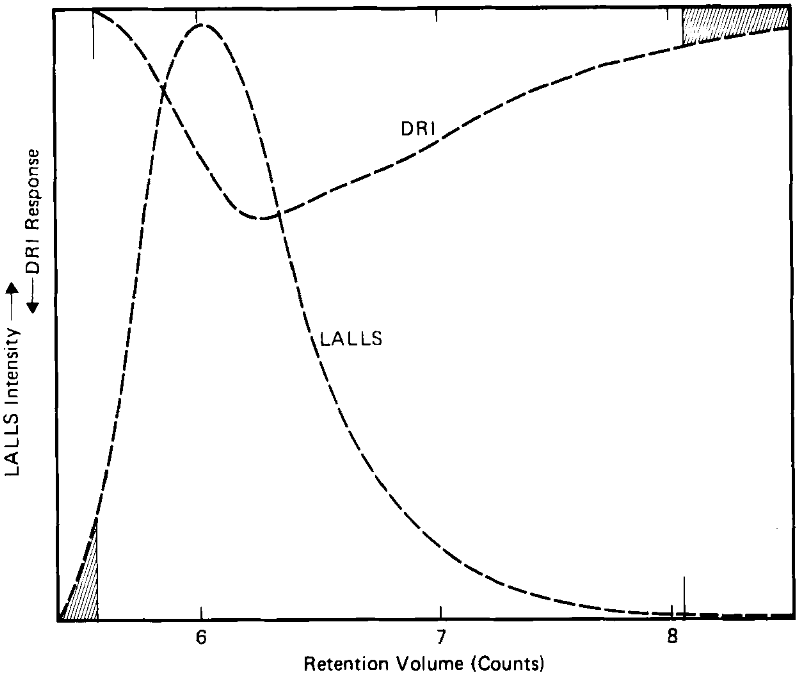

Fig. 9 Typical LALLS and DRI chromatogram of a broad molecular weight distribution samples. The shaded areas are regions where one of the detectors does not have sufficient sensitivity.

the problem of LALLS's extreme sensitivity in the high end of the MWD and lack of sensitivity in the low end of the MWD, we devised an electronic "black box" (herein referred to as DG) which allows one to change the sensitivity instantaneously at any point in the chromatogram while at the same time providing the exact values of G_o at each sensitivity setting.

An example of the application of the DG is shown in Fig. 10. To attain a higher sensitivity in the front end of the chromatogram (point A), the digital thumb wheel control of the DG is set at a high value of 4300 (high DG setting

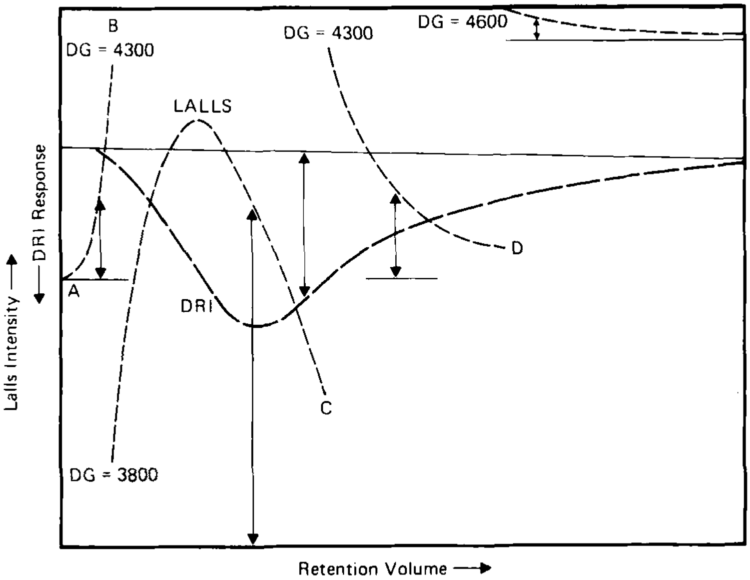

Fig. 10 Typical chromatograms where the sensitivity and the signal-to-noise ratio of the LALLS detector is changed at the various regions of the sample retention volume with the use of the DG device.

results in a high LALLS sensitivity and signal-to-noise ratio). As the concentration increases the LALLS response rises sharply and, to prevent over loading the photomultiplier tube, the DG setting is reduced to 3800 at point B. At point C the DG is returned to the high setting of 4300 and before it reaches the baseline it is raised to 4600 at point D. In this manner, the precision of the LALLS detector at all points in the chromatogram is increased, and permits the calculation of M_w at the low molecular weight end of the chromatogram (point D and beyond).

Since DG can be calibrated such that each DG reading corresponds to a G_o value, the Raleigh factor ($R_\theta = G_\theta/G_o$) can be calculated at all points of the LALLS chromatogram.

The G_o for all points in the LALLS chromatogram of Fig. 10 can be obtained from the DG calibration curve of Fig. 11. For example, the G_o from points A to B is 2.37×10^7, and between points B and C it is 1.33×10^7.

Figure 12 shows plots of the weight average molecular weights across the chromatograms of PVAC (synthesized at 60°C and [AIBN] = 10^{-5} g-mole/l) versus retention volume of various conversion levels. At least three important observations can be made from this figure:

1. At any retention volume, the M_w increases markedly with conversion. This is in accord with the well-known fact that branched polymers with the same hydrodynamic volume as linear polymers have higher M_w.

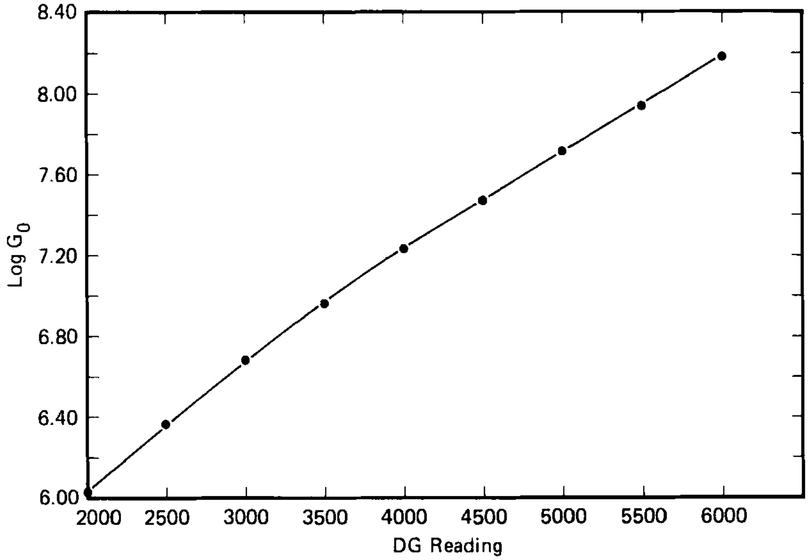

Fig. 11 A typical calibration curve for the DG device. This calibration curve permits direct conversion of the DG reaching to G_o, a quantity required for the calibration of the Rayleigh factor R_θ.

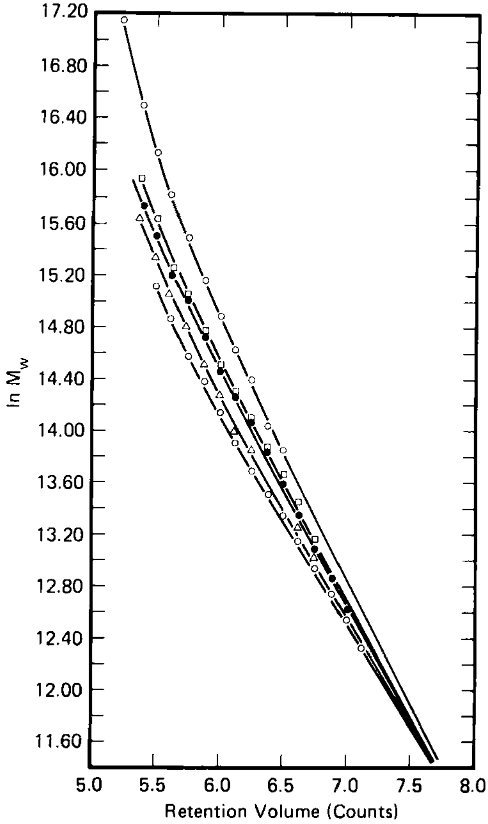

Fig. 12 A plot of the M_w as measured by the online GPC/LALLS system across the chromatogram of PVAC synthesized at 60°C, [AIBN] = 10^{-5} g-mole/l and at conversion levels of: ○ - 3.27%, △ - 30.7%, ● - 48.5%, □ - 57.0% and ○ - 90.6%.

2. The molecular weight at all conversion levels converges at larger retention volumes, i.e., greater than 7.5 counts. This is as expected since the frequency of branches per molecule decreases with decreasing molecular weight and since the lower molecular weight fraction of the high conversion PVAC would resemble the more linear PVAC of the low conversion level sample.

3. Since the frequency of branching is very large in free radical polymerized PVAC, the polydispersity of the PVAC samples at any retention volume in the LALLS and the DRI detector cells may be high, because polymers with different degrees of branching may have the same hydrodynamic volume (same retention volume) but possess widely different molecular weights.

These observations have important implications in regards to the use of the universal calibration curve for nonuniformly branched polymers and the interpretation of the MWD obtained by the GPC/LALLS technique. These implications will now be discussed.

Because the LALLS and DRI detectors sense eluted fractions which are polydisperse in molecular weight (although homogeneous in hydrodynamic volume), the computed value of the molecular weight at any retention volume is the weight average molecular weight, M_w. Thus, the molecular weight distribution obtained by the GPC/LALLS technique is, in fact, not the true MWD, but is a plot of the M_w across the chromatogram as shown in Figs. 12 and 14. Although these plots give a qualitative picture of the MWD of the samples, they should not be used to calculate molecular weight averages (M_N, $M_z \cdots$) other than $\bar{M}_w$. For example, if one were to calculate the M_N from the high conversion data of Figs. 12 and 14, the result would be an M_N which is too large relative to, let us say, an osmometer value.

Figures 12 and 14 show that M_w variation with retention volumes for PVAC samples prepared at 80°C over a range of conversion levels. On comparison, it appears that the ln M_w versus retention volume plot of the PVAC synthesized at higher temperature exhibits more severe curvature at lower retention volumes. This is an indication of higher LCB frequency in the 80°C sample. This observation confirms the virial coefficient A_2 and M_w shown in Fig. 4 for PVAC

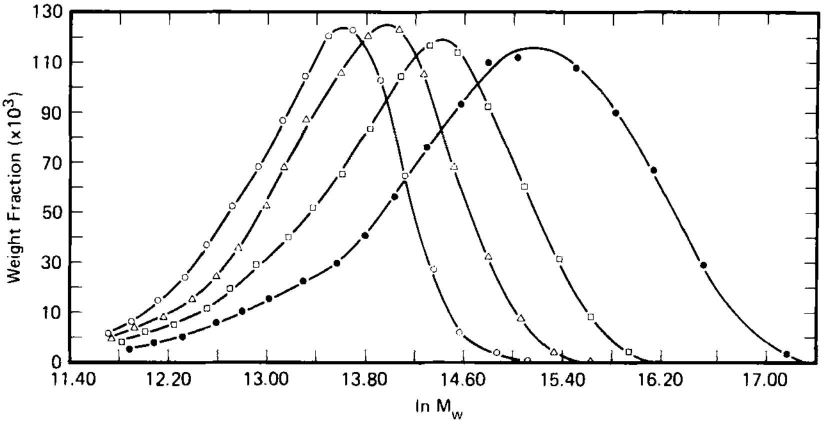

Fig. 13 A plot of the log M_w versus the weight fraction of the same PVAC samples shown in Fig. 12. The same symbols are used to represent the same percent conversion as in Fig. 12.

prepared at 60°C and 80°C, that is, samples prepared at the higher temperature have a higher LCB frequency. The differential MWD (weight fraction versus ln M_w) plots for the 60°C and 80°C PVAC are shown in Figs. 13 and 15. The shift of the distributions at higher molecular weights with conversion is as expected.

The problem of nonuniformly branched polymers being eluted into fractions which are polydisperse in molecular weight even though they possess the same hydrodynamic volume will now be considered. This problem makes the interpretation of MWD obtained by the universal calibration parameters (UCP) concept proposed by Benoit, et al (10) unclear. To correct for the molecular weight polydispersity of the fractions in the detector cells, earlier investigators (4,5,10,11) plotted the product of the intrinsic viscosity and the weight average molecular weight ($[\eta]M_w$). The use of M_w may also have been an attempt to correct for the fact that the polymer injected into the GPC was not monodisperse,

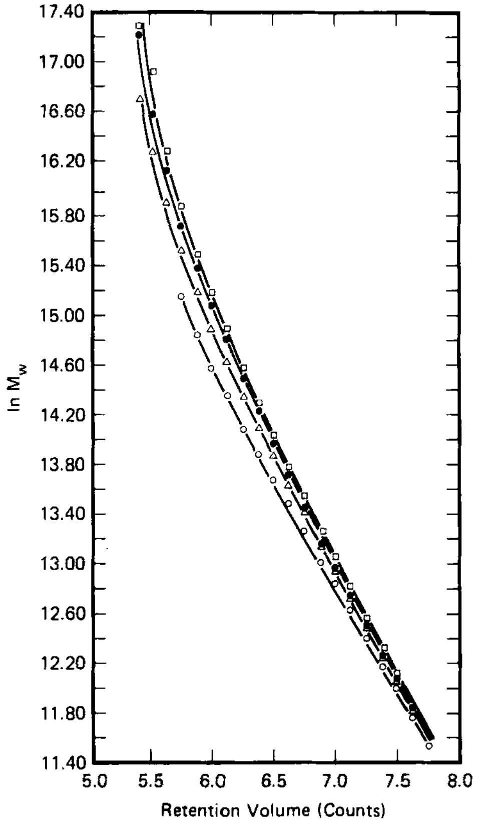

Fig. 14 A plot of the M_w as measured by the online GPC/LALLS system across the chromatogram of PVAC syntehsized at 80°C, [AIBN] = 10^{-4} g-mole/l and conversion levels of ○ - 31.7%, △ - 72.0%, ● - 80% and □ - 89.5%.

but a fraction with a significant spread in molecular weight. The choice of M_w as the proper molecular weight average to couple with the [η] for the UCP concept perhaps evolved from the intuitive feeling that for most polymers, M_w is the closet average to the viscosity average M_v. However, there are

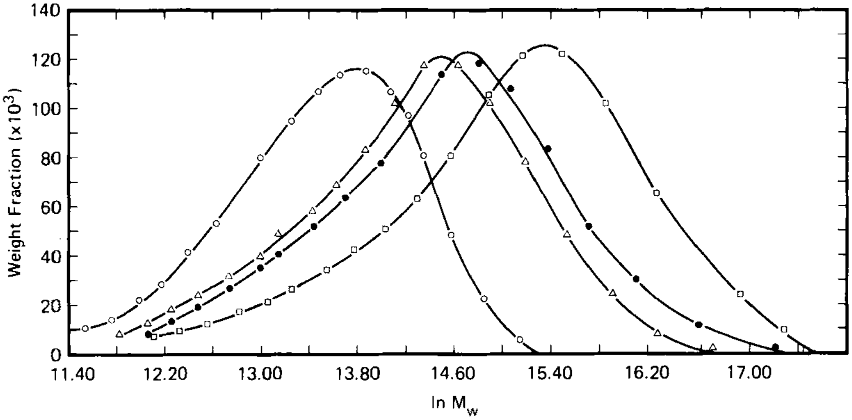

Fig. 15 A plot of the M_w versus weight fraction of the same PVAC samples and symbols shown in Fig. 14.

indications (4,5,12) suggesting that the choice of M_w for the UCP may be incorrect.

In Table I, compare the $[\eta]$ for all retention volumes with that of the whole polymer $[\bar{\eta}]$. It is clear that there is an inconsistency. The $[\eta]$ values found using the universal calibration curve based on polystyrene ($[\eta]_{ps}M_{ps}$) and the parameter $[\eta]M_w$ are too small relative to the whole polymer $[\bar{\eta}]$. This is particularly evident for sample E-5 which has a higher LCB frequency. The high precision of the M_w in Table I was verified by the excellent agreement between the $\bar{M}_w$ obtained from the integration of the M_w with respect to the weight fraction in Table I and the $\bar{M}_w$ obtained from offline LALLS measurement of both samples.

Perhaps a more direct and convincing proof of the inappropriateness of M_w and the correctness of M_N for the UCP concept is provided by the following theoretical analysis. If we assume that the polymer molecules eluted into the detector cell at any specified retention volume all have the

Table I Use of the universal calibration curve based on polystyrene to generate intrinsic viscosities across branched poly(vinyl acetate) chromatograms.

Retention Volume Counts	$(M[\eta])_{ps}$ $(x10^{-6})$	PVAC Sample - E1		PVAC Sample - E5	
		$M_w x10^{-6}$	$[\eta]$	$M_w x10^{-6}$	$[\eta]$
5.5	8.87	...	...	5.13	1.729
5.625	6.21	...	...	4.20	1.478
5.75	4.35	2.13	2.04	3.20	1.359
5.875	3.05	1.758	1.735	2.47	1.235
6.0	2.14	1.383	1.547	2.00	1.070
6.125	1.498	1.099	1.363	1.623	0.923
6.25	1.050	0.882	1.190	1.316	0.798
6.375	0.736	0.737	0.999	1.045	0.704
6.5	0.515	0.622	0.828	0.856	0.602
6.625	0.361	0.514	0.702	0.694	0.520
6.75	0.253	0.417	0.607	0.514	0.492
6.875	0.1773	0.344	0.515	0.442	0.401
7.0	0.1243	0.279	0.446	0.381	0.326
		$[\bar{\eta}]_{E1} = 2.20$		$[\bar{\eta}]_{E5} = 3.00$	

same hydrodynamic volume (this is true if we assume band spreading is negligible), we can write

$$[\eta]_{ps} M_{ps} = [\eta]_1 M_1 = [\eta]_2 M_2 = \cdots \quad (8)$$

where species 1, 2, ··· may refer to linear, branched, copolymers or blends of homopolymers. The $[\eta]$ in the detector cell is given by

$$[\eta] = W_1 [\eta]_1 + W_2 [\eta]_2 + \cdots \qquad (9)$$

where W_1, W_2, $\cdots$ are the weight fraction of the species in the detector cell. Equation (9) may be rewritten as

$$[\eta] = \frac{W_1}{M_1} [\eta]_1 M_1 + \frac{W_2}{M_2} [\eta]_2 M_2 + \cdots \qquad (10)$$

By virtue of Equation (8), Equation (10) can be written as

$$[\eta] = [\eta]_{ps} M_{ps} \left(\frac{W_1}{W_2} + \frac{W_2}{M_2} + \cdots \right) \qquad (11)$$

By definition, the number average molecular weight M_N is given by

$$M_N = \frac{1}{\frac{W_1}{M_1} + \frac{W_2}{M_2} + \cdots} \qquad (12)$$

Thus, the correct universal calibration parameter is given by

$$[\eta] M_N = [\eta]_{ps} M_{ps} = [\eta]_1 M_1 + [\eta]_2 M_2 + \cdots \qquad (13)$$

and the correct molecular weight average to use in the UCP is the number average molecular weight, M_N. The use a viscometer online with GPC would thus provide the variation of M_N across the chromatogram.

Unfortunately, a suitable online viscometer which can provide instantaneous intrinsic viscosities for both high and low temperature operation of the GPC is not available commercially. We therefore propose an indirect method to obtain the variation of intrinsic viscosity and M_N across a GPC chromatogram and an accurate measure to $\bar{M}_N$ of the whole polymer. The intrinsic viscosity - molecular weight relationship for a polymer with LCB is expressed as

$$\ln[\eta] = \ln K + a \ln M_N + b\,(\ln M_N)^2 + c\,(\ln M_N)^3 \qquad (14)$$

where K and a are Mark-Houwink constants for linear polymers. If M_{N_O} is taken as the cutoff molecular weight below which the polymer is linear,

$$b = -\,c \ln M_{N_O} \qquad (15)$$

we are now left with one unknown which is obtained using an independent measurement of the whole polymer intrinsic viscosity. The interactive procedure employed is to estimate the parameter c and use the universal molecular weight calibration curve based on polystyrene to determine the variation of $[\eta]$ with retention volume acorss the chromatogram. That is, integrate $[\eta]$ according to Equation (16) to determine the whole polymer instinsic viscosity $[\bar{\eta}]$,

$$[\bar{\eta}] = \quad F(V)\ [\eta](V)\ dv \qquad (16)$$

where F(V) is the normalized DRI response. Comparison of the measured and calculated $[\bar{\eta}]$ will permit the estimate of c to be improved until convergence is achieved. The result is the variation of M_N and $[\eta]$ across the chromatogram and then integration gives $\bar{M}_N$ of the whole polymer. Thus, the $[\eta]$ values may be used with a branching model to estimate LCB frequencies.

SUMMARY

We have demonstrated in this work that the LALLS and the online LALLS/GPC techniques are indeed powerful tools for the solution characterization of branched polymers. We have shown that the $\bar{M}_W$ and the weight fraction M_W distribution of polymers can be obtained rapidly and accurately, giving data that agree well with theory and data previously obtained for similar PVAC samples by Graessley (6) using conventional light scattering.

In the process of obtaining the best possible data for the online LALLS/GPC, we developed a "black box" device (designated DG) which optimizes the sensitivity and the signal-to-noise ratio of the LALLS photometer. The DG not only simplifies the operation of the LALLS, but also increases the dynamic range of the photometer for the M_w measurement. This feature allows the accurate measurement of the low M_w components of a sample with a broad MWD.

More importantly, we have unambiguously shown that the most commonly used universal calibration parameters $[\eta]\ M_w$ is incorrect, and the errors which can arise by using such a parameter to calculate either the molecular weight or the $[\eta]$ from the GPC chromatogram can be very large, particularly for polymers which possess the same hydrodynamic volume but have widely different molecular weights. The correct molecular weight average to use in the universal calibration parameter for GPC effluents which are heterodisperse in molecular weight is the number average molecular weight, M_N. Thus, we recommend that $[\eta]\ M_N$ be used as the generalized universal calibration parameter for GPC analysis of polymers with various molecular architectures, i.e., linear, branched, copolymers with compositional drifts and polymer blends.

Finally, we have proposed an indirect method to use with the universal molecular weight calibration curve to determine the weight fraction - M_N distribution and the $\overline{M}_N$ at the whole polymer.

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