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Determination of molecular weight and size distribution and branching characteristics of PVAc by means of size exclusion chromatography/multi-angle laser light scattering (SEC/MALLS)

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Abstract

SEC/MALLS has been applied for the determination of molecular weight and size distributions and to quantify branching in polyvinyl acetate (PVAc). Linear and branched samples obtained by solution and bulk polymerization were analyzed. The molecular weight distribution of the branched polymer was broader and the mean square radius was found to be smaller, 38.8 nm (with molecular weight of 770 000), than for the linear polymer, 42.3 nm (with molecular weight of 740 000). Branching characteristics could be determined by using Zimm and Stockmayer equations. It has been found that the number of branches for the branched sample increases from about 1 to 9, per molecule, with increasing molecular weight.

Keywords: SEC/MALLS; Random branching; Branching characteristics

1. Introduction

Molecular weights, molecular weight distributions and branching of polymers are crucial for product properties. The molecular weight distribution is one of the key structural characteristics, which can influence polymer physical properties, while the distribution of long-chain branches is of considerable importance for the rheological and morphological properties. The accurate measurement of the branching characteristics is known to be difficult. Usually in the papers g_M is shown but other then a great deal of scattering in the experimental data [1,20].

Size exclusion chromatography (SEC) provides a useful method for the determination of molecular weight distributions using calibration standards, i.e. narrowly distributed polymers with known molecular weights to establish the relationship between the elution volume and molecular weight. For linear polymers the method to determine the MWD based on a standard SEC elution curve is well established. However, for branched polymers the measured SEC data must be analyzed with additional means to provide information about branching. In SEC measurements polymer molecules are fractionated according to hydrodynamic volume. The size of branched polymer molecules is known to be smaller than that of linear ones having the same molecular weight [2]. Therefore, the true molecular weight cannot be obtained through the usual procedure. However, simultaneous measurement of light scattering intensity and concentration allows direct determination of the weight-average molecular weight of the eluted fraction, without calibration using the aforementioned standards. To identify long-chain branching, SEC can be coupled with a viscometer or laser light scattering detectors, such as low-angle laser light scattering (LALLS) or multi-angle laser light scattering (MALLS) detectors.

An alternative method to determine branching is ^{13}C NMR, but this technique does not yield information on the distribution of the degree of branching across the sample. Considering PVAc, Lowell et al. [32] showed that transfer to polymer, one of the mechanisms responsible for branching, can occur via the backbone tertiary C–H and the methyl side group. The latter one is dominant and it results in long-chain branches whether

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the former one yields short-chain branches. Our investigations will be focused primarily on the determination of long-chain branching.

Using SEC coupled with a viscometer, molecular weight distributions, intrinsic viscosity distributions and long-chain branching as a function of molecular weight were reported for polymer standards and commercial polymers [3–9]. Hu et al. has determined the radius of gyration by combining SEC with a viscometer and they found good agreement with results obtained from light scattering [10]. In all cases the combination of SEC with light scattering is employed as the reference method. Light scattering has long been a valuable analysis technique for macromolecular solutions and suspensions, since it provides absolute measurement of molecular masses and structural parameters of polymers across a wide range of molecular weights. Combined with SEC, light scattering yields weight-average molecular weight, M_w, and the corresponding z-average square radius RMS radius, of the eluted fractions. The SEC/MALLS coupling has made it possible to analyze the distributions of highly polydisperse samples and to obtain details of branching and molecular conformation. It is also possible to obtain both differential and cumulative distributions of the molecular weight and the mean square radius [11–13].

A few limitations of the coupled SEC/MALLS technique should be mentioned. Theoretically, light scattering measurements can detect sizes down to about a 20th of the incident wavelength. For a given concentration the scattered light signal is proportional to cM_w, where c is concentration of the solution and M_w, the weight average molecular weight. Hence, for molecular weights below a few thousand, relatively high concentrations are required to produce a detectable LS signal. In addition, the combined techniques require determination of the mass concentration for each eluting fraction either in parallel or in series. Accurate knowledge of dn/dc is also needed for the correct interpretation of light scattering data. However, despite these problems LS represents the most accurate and powerful molecular weight measuring device in combination with SEC. SEC/MALLS is absolute and it does not need prior calibration of columns. When SEC is combined with a differential viscometer (DV), calibration is usually required [11].

SEC/MALLS has been applied for the determination of molecular weights and molecular weight distributions of starches [14,15] and proteins [16,17]. For synthetic polymers, especially for branched ones, the technique is still in development. It has been shown for a polyethylene standard that a low-angle laser light scattering photometer in conjunction with a concentration detector and SEC can provide relatively fast and accurate determinations of long-chain branching as a function of molecular weight [18]. For two standard polyethylenes (IUPAC Alpha and NBS 1476) Tackx and Tack were the first to use SEC/MALLS and the universal calibration principle to determine the branching indexes g', g and the structural parameter b. These results were compared with SEC/DV measurements and good agreement was observed [19]. The combination of SEC with a MALLS detector will yield the absolute molecular weight, the root mean square radius (RMS) and the branching parameters. Also, in this way some information useful for the interpretation of the results obtained with conventional SEC can be gained. This was applied for narrow and broad standards of PS and PMMA, as well as for alkyd and phenoxy resins and derivatized and underivatized polyvinyl sugars by Podzimek [20]. Podzimek et al. used the SEC/MALLS technique, to investigate the presence of branched molecules by plotting the molar mass versus the elution volume and the RMS radius versus the molar mass for bisphenol—A based epoxy resins [21]. It has been shown by Podzimek et al. shown that highly branched and very large molecules can coelute together with smaller molecules in the region of high elution volumes and can cause retardation during SEC separation as a result of the macromolecular entanglement [22]. The branching numbers per molecule for randomly 3- and 4-armed branched PS's were determined from the ratio of the RMS radius of branched and linear PS with the same M_w by Kawaguchi et al. [23]. Size exclusion chromatography with an on-line light scattering detector was used for studies of microgel formation [24,25] and aggregation of humic acid [26]. Attempts have been made to achieve absolute molar mass detection by coupling SEC with membrane osmomotry. For this purpose a membrane osmometer based on a concentric design with a capillary-shaped membrane has been used. However, some problems such as a increased noise level at high-pressure and peak broadening still have to be solved [27].

The intention of this study is to demonstrate the applicability of SEC/MALLS technique for the characterization of polyvinyl acetate (PVAc). This method can provide absolute values of the molecular weight, the RMS radius and branching characteristics, independent of the chromatographic conditions, the elution volumes or the extent of sample interaction with the column support. Until now, attempts to determine branching characteristics for PVAc have been undertaken by Graessley et al. [28], who used a light scattering detector on non-fractionated samples to construct a Zimm plot. Our work constitutes the first time MALLS being coupled with SEC for determination of branching in PVAc.

2. Experimental

2.1. Materials

Vinyl acetate (MERCK) was purified prior to the synthesis. Purification was done by vacuum distillation at 40 °C and collecting the middle fraction. 2,2′-Azobis-izobutironitrile (AIBN 98%), (ACRŌS), was used as an initiator without purification. The solvent *t*-butanol (MERCK) was also used without purification.

2.2. Polymerization procedure

A number of branched PVAc samples and one linear were synthesized. One of the branched samples was synthesized by solution polymerization with a molar solvent/monomer ratio of 2. The solutions of distilled monomer, solvent and initiator ($[I]_0 = 1 \times 10^{-3}$ mol/l) were placed in a round bottom flask and degassed in several cycles: (1) freezing in liquid nitrogen; (2) vacuuming of the flask; (3) sealing from the vacuum pump and (4), thawing. These cycles were repeated several times. The reaction temperature was 60 °C ± 1 °C and the reaction time 5 h. The other two branched samples were synthesized by bulk polymerization under the same conditions as the previous sample but without the solvent. A linear sample was prepared by bulk polymerization in the same manner as the branched samples but with lower initiator concentration ($[I]_0 = 4 \times 10^{-5}$ mol/l. Polymerization was stopped when about 4% conversion was expected [29]. The obtained polymers were first dissolved in acetone and precipitated in distilled water at room temperature. Samples were dried in a vacuum oven at 50 °C until a constant mass was reached. Conversion of the polymers was determined gravimetrically. In the subsequent text linear PVAc will be denoted as a sample 1, branched PVAc obtained by solution polymerization is sample 2 and the two branched PVAc samples obtained by bulk polymerization are samples 3 and 4.

2.3. Measurements

The chromatographic system was a Waters 2690 Separation Module consisting of a pump, an Alliance autosampler, and a Waters 410 Differential Refractometer. One column, PLgel 5 μ, 10^5 Å 300 × 6.8 mm from Polymer Laboratories was used. The column was kept at 30 °C by a thermostat. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 ml/min. Prior to use THF was filtered over a filter with pore size 0.2 μm. The column was calibrated using polystyrene standards with molecular weights in the range of 374–3 350 000 g/mol (Polymer Standard Service-USA, Inc, with PDI for 1.03–1.05).

The light scattering instrument, a DAWN DSP multi-angle laser light scattering detector from Wyatt Technology, operating at 488 nm, was placed between the SEC and the refractive index detector. The DAWN detector was calibrated with toluene and normalized using the polystyrene standard with molecular weight of 30 000 g/mol. The d*n*/d*c* values for PS and PVAc are: 0.185 and 0.052 ml/g, respectively [30].

3. Results and discussion

3.1. Determination of molecular weights and molecular weight distributions

It is known that branched polymers are formed during free radical polymerization of vinyl acetate at mild conditions. Two mechanisms are held responsible for the creation of long branches: chain transfer to polymer and terminal double bond propagation. Terminal double bonds result from disproportionation or transfer to monomer [31]. The precise nature of all reactions involved and the location at the backbone to which the long branches are attached are still a matter of dispute [32]. The detection method for branches used here cannot distinguish between long branches made in either way nor does it yield information on the position of the branches. Therefore, we will not discuss this issue further. However, we are currently developing a sophisticated model to predict molecular weight and degree of branching distributions (MWD/DBD) from kinetic mechanisms. Comparing MWD/DBD results from the model to experimental data obtained in the present study may *indirectly* contribute to better information on the relative importance of the branching mechanisms mentioned.

Size-exclusion chromatography is an excellent technique for the separation of macromolecules according to size, as well as for the determination of molecular weights and molecular weight distributions. The molecular weight analysis of branched polymers is very difficult and often inaccurate when SEC is used with a concentration detector. A branched polymer of a given molecular weight has a smaller hydrodynamic volume than the corresponding linear one with the same molecular weight. For appropriate calibration, calibrants of the same molecular weight and with the same degree of branching and the same conformation would be needed. It is almost impossible to meet these requirements for reference materials. For PVAc such standards are not available, which makes conventional SEC inapplicable. In order to show differences in values of molecular weights for branched polymer obtained with conventional SEC and SEC/MALLS we have performed the above mentioned analysis on PVAc samples. Table 1 shows

Table 1
Molecular weights and RMS radii for PVAc samples obtained by conventional SEC and SEC/MALLS measurements

Sample	SEC		SEC/MALLS	
	M_w (g/mol)	M_n (g/mol)	M_w (g/mol)	$\langle r \rangle^2$ (nm)
1	579 000	64 300	740 000	42.3
2	594 000	336 000	770 000	38.8
3	1 024 000	121 000	2 570 000	142
4	1 091 000	154 000	1 666 000	60.2

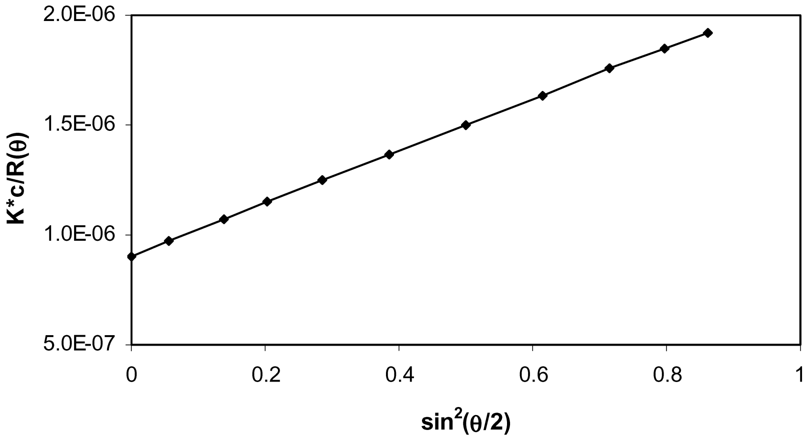

Fig. 1. Zimm plot for linear PVAc second order data fit.

molecular weights of linear and branched PVAc samples, obtained by conventional SEC.

The use of SEC coupled with MALLS gives direct access to both the absolute weight-average molecular weight and the root mean square radius for each slice across a sample peak of the SEC curve. It is assumed that each slice contains molecules of a single molecular weight, or at least a very narrow distribution.

The molecular weight for each slice is calculated according to the Zimm and Stockmayer equation [2,11,33]:

$$\frac{R_\Theta}{K^*c} = MP(\Theta) - 2A_2cM^2P^2(\Theta) + \cdots \qquad (1)$$

where:

R_Θ is the excess Rayleigh ratio,
$P(\Theta)$ is the particle scattering factor. $P(\Theta)$ is approximately equal to $1 - 2\mu\langle r^2\rangle/3! + \cdots$, where $\mu = (4\pi/\lambda)\sin(\Theta/2)$
c is the concentration of the polymer particles (g/mol),
M is the weight-average molecular weight,
A_2 is the second virial coefficient (ml mol/g^2), and
K^* is a constant. For vertically polarized incident light with a wavelength λ_0 in vacuum, K^* is given by:

$$K^* = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_A}\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2 \qquad (2)$$

where n_0 is the refractive index of the solvent at wavelength λ_0, N_A is Avogadro's number and dn/dc is the specific refractive index increment of the polymer.

The concentration of the polymer is measured for each slice using a refractive index detector. A plot of $R_\Theta/(K^*c)$ or $(K^*c)/R(\Theta)$ vs. $\sin^2(\Theta)$ is constructed at each retention time which gives the molecular weight and RMS radius distributions. M can be directly determined from the intercept at zero angle, whereas, the slope yields the mean square radius [11]. If the concentration is sufficiently small than $A_2c = 0$, and Eq. (1) is solved for $A_2 = 0$, than for the molecular weight and RMS radius one obtains the following equations:

$$M = \left(\frac{K^*c}{R_0}\right)^{-1} \qquad (3)$$

and for $\langle r^2\rangle^{1/2}$:

$$\langle r^2\rangle^{1/2} = \frac{\sqrt{3\lambda_0}}{4\pi n_0}\sqrt{m_0M} \qquad (4)$$

After separation of the polymer has been performed and the collected data have been processed, characteristic averages of the molecular weight and the moments of the RMS radius can be calculated for each peak in the elution curve by using the formulas presented elsewhere [11].

For accurate calculation of molecular weights and RMS radii it is very important how extrapolation of the plot R_Θ/K^*c vs. $\sin^2(\Theta/2)$ (Debye plot) or the plot $(K^*c/R_\Theta$ vs. $\sin^2(\Theta/2)$ (Zimm plot) to zero angle is performed and which fitting degree is applied. This can dramatically affect the end results. Therefore, it should be approached with great care. So far, several authors have addressed this problem for different polymers, mostly working with PMMA and PS [11,16,20,34]. In this paper problems associated with the extrapolation and fitting for the case of PVAc will be considered. For molecules up to a molecular weight of about 500 000, a straight line (first-order polynomial) is adequate. For higher molecular weights higher order fits must be used.

The extrapolation and fitting procedures for the linear PVAc sample was done by using a plot of R_Θ/K^*c vs. $\sin^2(\Theta/2)$, with a second order fit and plots of K^*c/R_Θ vs. $\sin^2(\Theta/2)$ with first and second order fits, respectively. It was obvious that Debye plot was not even linear, whereas, the Zimm plots are linear, both for first and the second order fit. This suggests that a Zimm plot, even with first order fitting (Fig. 1) is the proper plot for the calculation of molecular weights of the linear PVAc samples. The same is valid for the branched sample number 2.

The linearity of the K^*c/R_Θ vs. $\sin^2(\Theta/2)$ plot is a great advantage, because the use of R_Θ/K^*c vs. $\sin^2(\Theta/2)$ plots for broad-distribution samples may require a higher polynomial

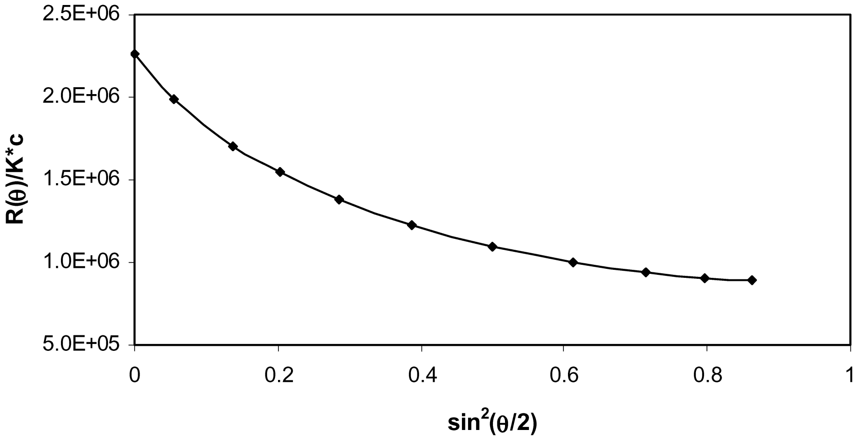

Fig. 2. Debye plot for branched PVAc (sample 4) 4th order data fit.

order to fit the light scattering data in different parts of the chromatograms [11,20]. For molecular weights of about 2 000 000, Debye ($R_{\Theta}/K^{*}c$ vs. $\sin^2(\Theta/2)$) plot should be used with a higher polynomial degree. For the samples obtained by bulk polymerization (3 and 4) for which we suspected that molecular weights exceed one million, Debye plots with higher order fits were used. Debye and Zimm plots with 4th order fitting were investigated for sample 4. For this sample with molecular weight approaching 2 000 000, Zimm plots are no longer linear and it is better to use Debye plot (Fig. 2), even if it is with higher order fit. In conclusion, for low molecular weights, both Zimm and Debye plot are linear and appropriate. For moderate molecular weights (which is the case for PVAc samples 1 and 2) Zimm plots are linear and requires lower order fitting than Debye plots. For higher molecular weights (PVAc samples 3 and 4) Zimm plots are not linear and the error for RMS radius is higher than the error obtained by using Debye plot and therefore it is better to use Debye plot with higher order fit.

Molecular weight distributions for the linear sample 1 and the branched samples 2, 3 and 4 are given in Fig. 3.

Fig. 3 clearly shows that the linear sample has a narrower distribution than the branched samples. The broadening and the shoulders at higher molecular weights are due to branching. Plots of the molecular weight versus the elution volume for the linear sample 1 and branched sample 2 are shown in Fig. 4. The curves for the samples almost coincide at the same elution volumes at lower molecular weights, but at higher molecular weights they deviate. This deviation is due to the presence of branches. Branched molecules are more compact than linear ones and therefore they have smaller sizes when molecular weights are equal. Long chain branching contributes significantly to the higher molecular weights. So that highly branched molecules have relatively higher molecular weight. If a linear sample with the same molecular weight as the branched one is not available, we can still identify which sample is more branched by just comparing two branched samples. This was done for samples 3 and 4 and it was found that sample 3 has higher molecular weights at the lower elution volumes than sample 4, which indicates that sample 3 is more branched than sample 4 (Fig. 5).

Molecular weights obtained with the SEC/MALLS technique for the linear and branched samples are given in Table 1. Note that Table 1 shows data for the *weight*

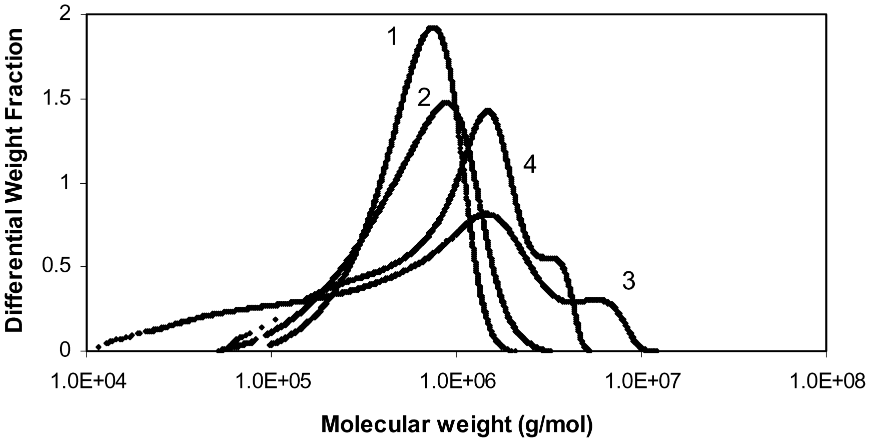

Fig. 3. Differential molecular weight distribution of: 1-linear PVAc, 2-branched PVAc sample obtained by solution polymerization, 3- and 4-branched PVAc samples obtained by bulk polymerization.

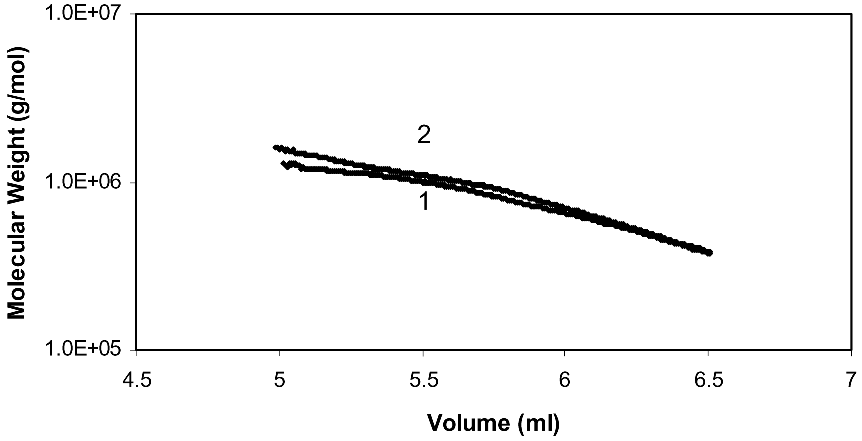

Fig. 4. Molecular weight vs. elution volume for 1-linear PVAc and 2-branched PVAc obtained by solution polymerization.

average of the molecular weight and the *z average* of the RMS radius. Marked differences are observed between the values of molecular weights obtained with SEC only and with SEC coupled with MALLS. The reason for this is the occurrence of peak broadening in the SEC instrument, which causes each slice to contain a non-monodisperse mixture. As a result of this effect, SEC with MALLS has a tendency to overestimate the n average molecular weight, in spite of these broadening effects, we may in practice still make the assumption that each slice is monodisperse [20].

3.2. Determination of RMS radius

The results for the RMS radius as well as for the molecular weights were obtained by using the middle section of the elution peaks, in order to decrease polydispersity of the samples. This is necessary, since the most accurate light scattering results are obtained for nearly monodisperse samples. By taking only the middle part of the peak, molecules at the tails of the peak with very low and very high molecular weights are discarded [11,19,20,34]. Very low molecular weights cannot be measured by this technique because the limitation of MALLS (RMS radius ≥ 15 nm). Aggregates or micro gels can be detected with light scattering, but not with the differential RI detector, because their concentration is very low. Even though the polydispersities of the samples used here were 1.5 for the linear sample and 1.8 for the branched one, the species at both ends of the peak should be still neglected. The plot of RMS radius versus molar mass is given in Fig. 6. This confirms that the branched polymer has a smaller RMS radius than the linear one at the same molecular mass. The slope of the line for the linear sample is 0.57 and for the branched one 0.39. This compares well to known values for linear random coils, being in the range 0.5–0.6 [11]. A lower value for the slope is indicative of the existence of branches. Concerning the samples obtained by bulk polymerization, Fig. 7 shows that sample 3 is more branched than sample 4. Values obtained for the RMS radii of linear and branched samples are given in Table 1.

3.3. Determination of branching characteristics

A fundamental model for the determination of branching has been derived by Zimm and Stockmayer [2]. It can be used for the determination of branching in polymers from

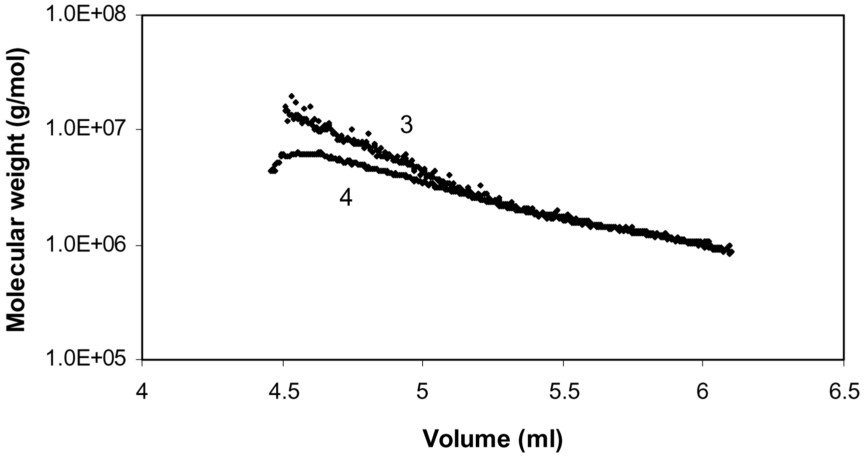

Fig. 5. Molecular weight vs. elution volume for 3 and 4-branched PVAc obtained by bulk polymerization.

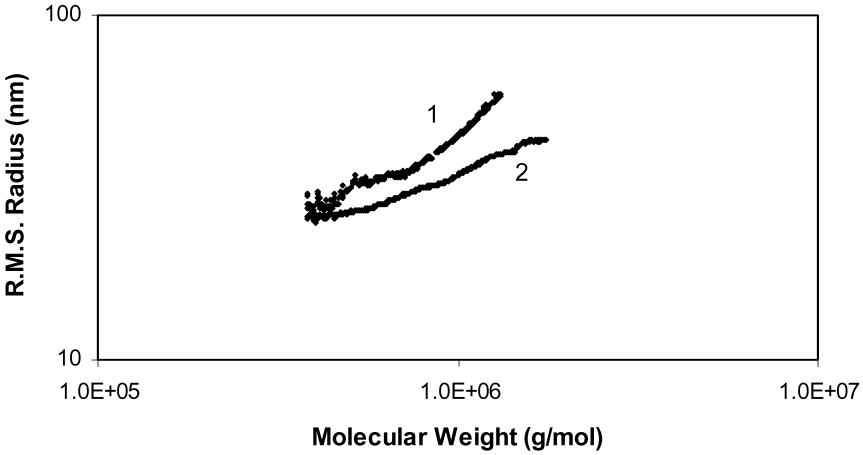

Fig. 6. Conformational plot (R.M.S. radius vs. molecular weight) for 1-linear PVAc and 2-branched PVAc obtained by solution polymerization; slopes of conformation plots are 0.57 and 0.39 for linear and branched sample, respectively.

molecular weight and RMS radius data obtained by SEC/MALLS. The branching ratio, g_M, is defined simply as the ratio of the mean square radius of the branched polymer, $\langle r^2\rangle_{br}$ to that of the linear polymer, $\langle r^2\rangle_{lin}$, at the same molecular weight [2]:

$$g_M = \left(\frac{\langle r^2\rangle_{br}}{\langle r^2\rangle_{lin}}\right)_M \tag{5}$$

This is the so-called radius method. The measured branching ratio g_M as calculated from the RMS radii of the linear and branched samples, 1 and 2, respectively, vs. molecular weight is given in Fig. 8. This graph shows that g_M becomes lower, from about 0.95 for low molecular weights until 0.55, as the molecular weight and branching increases. Finally, a practical issue should be mentioned here. In order to obtain a value for g_M from experimental RMS radius data of linear and branched polymers, the molecular weights of both polymers should be the same. Hence, branching ratios can only be calculated for overlapping sections of the MW regions of linear and branched polymers. Branching ratio can be determined also by using mass method (using ratio between molecular weights of linear and branched polymer at the same elution volume, Eq. (6)).

$$g_M = \left(\frac{M_{lin}}{M_{br}}\right)_V^{\frac{(\alpha+1)}{\varepsilon}} \tag{6}$$

But in the case of using mass method draining parameter ε should be known, which is generally unknown. Usually, for polymers is 0.5–1 [35]. This broad range makes this method uncertain. Therefore, we used only the radius method in our calculations.

Another important branching characteristic that can be calculated by using SEC/MALLS techniques is the number of branches per molecule. The relation between the number of branches per molecule and the branching ratio depends on the branching functionality and the polydispersity of the sample of branched molecules. Assuming PVAc is a tri-functional randomly branched polymer, the Zimm and

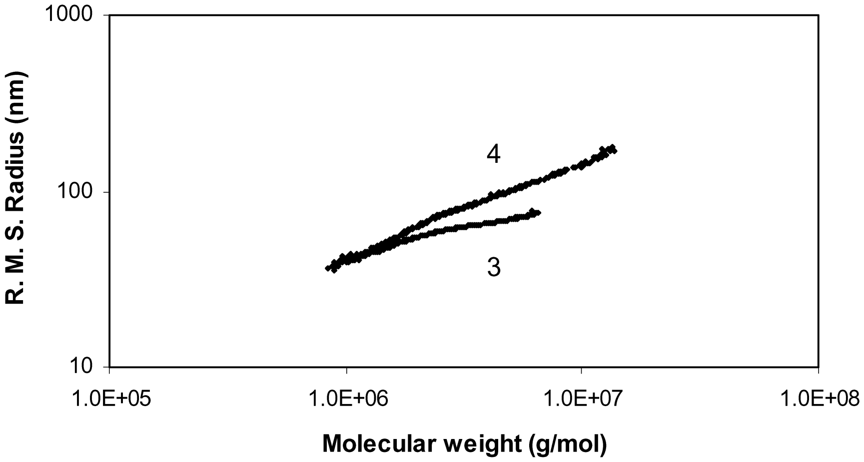

Fig. 7. Conformational plot (R.M.S. radius vs. molecular weight) for branched PVAc samples 3 and 4 obtained by bulk polymerization.

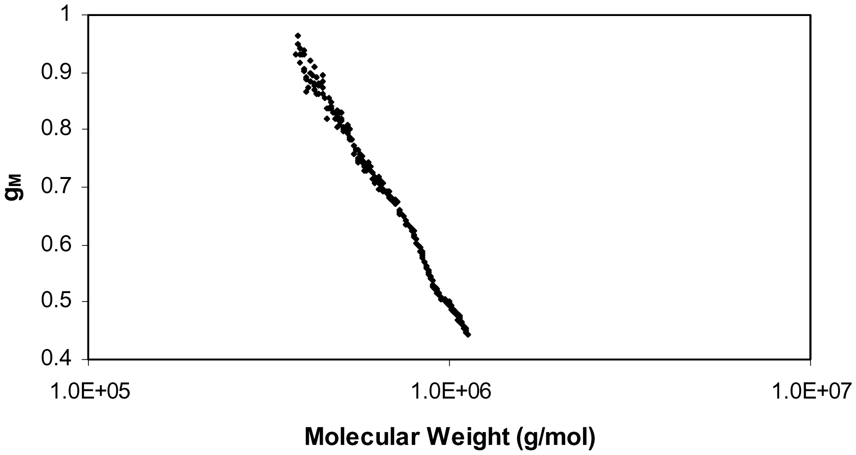

Fig. 8. Branching ratio, g_M, as a function of molecular weight for randomly branched PVAc sample calculated by radius method.

Stockmeyer [2] expressions are:

$$\text{polydisperse}: g_M = \frac{6}{B_{3w}} \times \left\{ \frac{1}{2}\left(\frac{2+B_{3w}}{B_{3w}}\right)^{1/2} \ln\left[\frac{(2+B_{3w})^{1/2}+B_{3w}^{1/2}}{(2+B_{3w})^{1/2}-B_{3w}^{1/2}}\right] - 1 \right\} \quad (7)$$

$$\text{monodisperse}: g_M = \left[\left(1+\frac{B_{3n}}{7}\right)^{1/2} + \frac{4B_{3n}}{9\pi}\right]^{-1/2} \quad (8)$$

Here, B_{3w} is the weight average number of branches per molecule of a polydisperse sample, while B_{3n} is the number of branches per molecule of a monodisperse sample. In these two relations, the left-hand side, g_M, has been calculated from the experimental RMS radii. The most used formula is the one for a polydisperse sample, since each fraction in the SEC chromatogram is considered to be polydisperse due to the co-elution of linear and branched species. Extensive investigations by Greassley et al. suggest that Eq. (7) is the most appropriate for calculation of number of branches of PVAc [36]. However, it may be argued that Eq. (8) is more suitable to the narrow fraction eluted from a SEC column. Because the differences between the results obtained from the two equations are minor, we decided to use the Eq. (7). The resulting number of branches is plotted vs. M_w in Fig. 9. The number of branches range from 1 until 9 for higher molecular weights.

From the number of branches, the long chain branching frequency can be calculated, defined as the number of branches per 1000 repeat units:

$$\lambda = 1000B\frac{R}{M} \quad (9)$$

where B is the number of branches per molecule for each slice, R is the repeat unit molecular weight and M is the molecular weight.

The long chain branching frequency calculated from the number of branches using Eq. (9) is plotted versus the molecular weight in Fig. 10. For the molecular weight of 800 000 PVAc contains 0.4 branches per 1000 monomer units. From Figs. 9 and 10 it is clear that the number of branches per molecule and the long chain branching frequency increase with molecular weight. Available data for LDPE show the same general trend, although discrepancies exist between different sources [37].

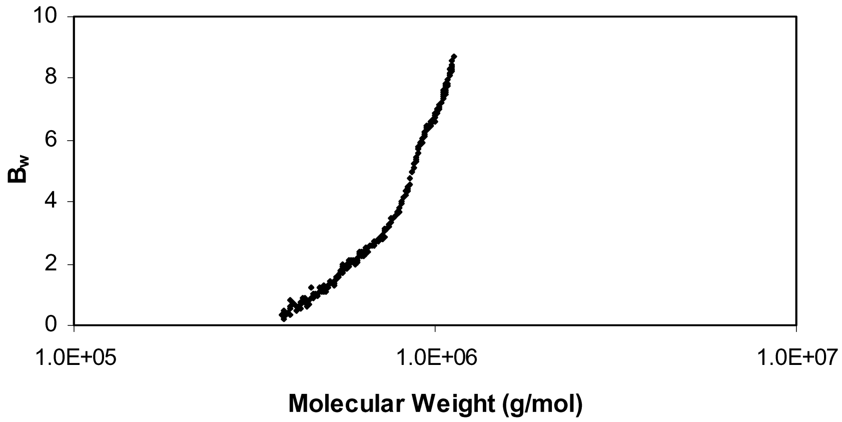

Fig. 9. Number of branches, B_w, as a function of molecular weight for randomly branched PVAc.

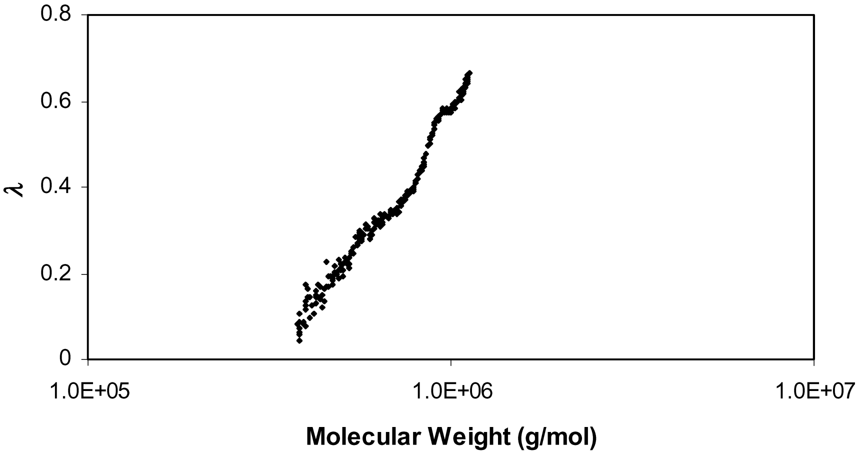

Fig. 10. Long chain branching, λ, as a function of molecular weight for randomly branched PVAc.

Branching characteristics for branched samples 3 and 4 were not determined although an overlapping region exists, where molecular weights of branched and linear sample are the same. The reason for this is the fact that molecular weights are overlapping at around one million. The molecular weights about 1 000 000 for the linear sample are located at the tail of the peak with high molecular weights where there is a big possibility of existence of certain number of branches [19]. Therefore, it is not impossible that in the overlapping region the linear sample is equally or even more branched than the sample 3 and 4 in their low molecular weight regions.

4. Conclusion

SEC/MALLS is a convenient technique for the determination of molecular weight, size of macromolecules and branching characteristics. SEC allows fractionation of the sample and MALLS allows determination of absolute molecular weights and RMS radii. Branching characteristics, the branching ratio, the number of branches per molecule and the long chain branching frequency, are obtained by using the theory of Zimm and Stockmeyer. Disadvantage of a SEC/MALLS combination is the limitation concerning the size of the molecules that can be measured. The molecules subject to investigation should be larger than 15 nm in radius. Species with very high molecular weights such as aggregates or micro gels can also cause problems, because their concentration is to low for them to be detected with the differential RI detector.

However, for the determination of the molecular weigh and molecular weight distribution, as well as the branching characteristics is much better to use SEC/MALLS than MALLS only, because by coupling these two techniques the limitation of the characterization of the polydisperse nonfractionated polymers are avoided.

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