Characterization of Branched Polymers by SEC Coupled with a Multiangle Light Scattering Detector. II. Data Processing and Interpretation

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ABSTRACT: This study deals with the characterization of branched polymers by means of size-exclusion chromatography coupled with a multiangle light scattering detector (SEC-MALS). The application of SEC-MALS is demonstrated on several randomly branched polystyrene and star-branched poly(benzyl methacrylate) samples. Various methods of the data processing are compared. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 454–460, 2001

Key words: size-exclusion chromatography; light scattering; branching

INTRODUCTION

A branched polymer is a polymer composed of molecules containing some units whose functionality exceeds two. Branched molecules can be synthesized by sophisticated procedures, providing tailored macromolecules with uniform structure or reactions resulting in randomly (statistically) branched polymers (e.g., polycondensation of a mixture of two and more functional monomers; radical copolymerization of a mixture of vinyl and divinyl monomers; branching of linear polymers by chemical reaction, heat treatment, or irradiation; radical polymerization with chain transfer to polymer). Unwanted branching often can occur as a result of various side reactions (e.g., the addition of glycols and water on double bonds of unsaturated acid or polymerization of double bonds during the manufacture of unsaturated polyester resins; chain transfer to the polymer during the synthesis of linear polymers by radical polymerization; addition of secondary hydroxyl groups on epoxy groups during the preparation of epoxy resins; and polymerization of difunctional monomers containing multifunctional impurities).

Branching may influence thermodynamic interactions between the polymer and solvent,[1–3] rheological properties,[4,5] Θ temperature,[2,6] glass-transition temperature,[7] melting behavior and crystallization,[8] phase separation of polymer mixtures,[9,10] curing behavior of synthetic resins,[11] mechanical properties, solubility, chemical resistance, and solution viscosity. In some cases the branching can have counteracting impact; for example, the change of glass-transition temperature with increasing degree of branching is the result of two effects: the increased number of end groups increases the chain mobility and free volume, whereas the introduction of branch points reduces the chain mobility and free volume.

Typical features of randomly branched polymers are the broadening of the molar mass distribution related to corresponding distribution without branching, and substantial amount of lin-

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ear molecules even in highly branched samples. In randomly branched polymers, the number of branch units in a polymer chain increases with increasing molar mass, and branching results in a high molar mass tail of the molar mass distribution.

A branched polymer sample is characterized by the branching ratio g_M, defined as the ratio of the mean square radius (R^2) of branched (*br*) and linear (*lin*) polymer at the same molar mass[12]:

$$g_M = \left(\frac{R^2_{br}}{R^2_{lin}}\right)_M \tag{1}$$

Formulas for this ratio of various branched polymer molecules have been calculated theoretically.[12] The branching ratio can be used for the calculation of the number of branch units per molecule.[12]

At constant molar mass, the root mean square (RMS) radius (radius of gyration, R) decreases with increasing degree of branching. Thus, the comparison of RMS radii and molar masses of particular samples can give information about the degree of branching. However, application of classical light scattering, which yields weight-average molar mass (M_w) and z-average RMS radius (R_z), is limited to polymers with a narrow molar mass distribution, because in samples with a broad molar mass distribution, the z-average RMS radius is affected more by high molar mass branched fractions than the weight-average molar mass. Therefore, the decrease of R_z resulting from the branching can be partially or even completely compensated by the increase of R_z resulting from the presence of high molar mass branched fractions. This compensation makes the characterization of branching of a polydisperse polymer by the classical light scattering measurement impossible. An alternative approach to the determination of branching ratio is the calculation using intrinsic viscosity $[\eta]$. The calculation is based on the Flory–Fox equation[13]

$$R = \frac{1}{\sqrt{6}}\left(\frac{[\eta]M}{\Phi}\right)^{1/3} \tag{2}$$

where Φ is the Flory constant and M is the molar mass. Using eq. (2), g_M can be expressed as

$$g_M^{3/2} = \left(\frac{[\eta]_{br}}{[\eta]_{lin}}\right)_M \tag{3}$$

Zimm and Kilb[14] showed that the exponent has the values of 0.5 for a nondraining polymer and 1 for a free-draining polymer. Therefore, eq. (3) can be written in more general form:

$$g_M^e = g'_M = \left(\frac{[\eta]_{br}}{[\eta]_{lin}}\right)_M \tag{4}$$

where the exponent e depends on the draining properties of a polymer coil.

Combination of size -exclusion chromatography (SEC) with a multiangle light scattering (MALS) detector has been shown to be a powerful method of the investigation of branching.[15–19] SEC-MALS measures the molar mass and RMS radius at each volume slice, which overcomes the limitation of classical light scattering, because the RMS radii and molar masses are obtained for almost monodisperse fractions.

EXPERIMENTAL

The chromatographic system consisted of a 600 pump (Waters, Milford, MA), a 717 autosampler (Waters), a set of two Styragel HR 5E 300 × 7.8 -mm columns (Waters), a light scattering detector miniDAWN (Wyatt Technology Corp., Santa Barbara, CA), and a 410 differential refractometer (Waters). Tetrahydrofuran (THF) was used as a mobile phase at a flow rate of 1 mL/min. ASTRA (Wyatt Technology Corp.) and Millennium (Waters) were used for data collection and processing. For the determination of molar mass by conventional SEC, the columns were calibrated by polystyrene standards (Polymer Laboratories, Church Stretton, Shropshire, UK) covering the molar mass range of 1000–4,340,000 g/mol.

Intrinsic viscosities were measured by means of a Ubbelohde viscometer at 25°C in THF.

Samples of randomly branched polystyrene (PS) were prepared by solution polymerization of styrene/divinylbenzene (DVB) mixtures containing various DVB concentrations. Samples of star-branched poly(benzyl methacrylate) (PBZMA) were prepared by group transfer polymerization of benzyl methacrylate with ethylene glycol dimethacrylate and isolation of branched fractions by precipitation. The molar mass of PBZMA branches was in the range of 4000 to 8000 g/mol.

The intrinsic viscosities of linear polymers were calculated using the following constants of the Mark–Houwink equation: a = 0.717, K

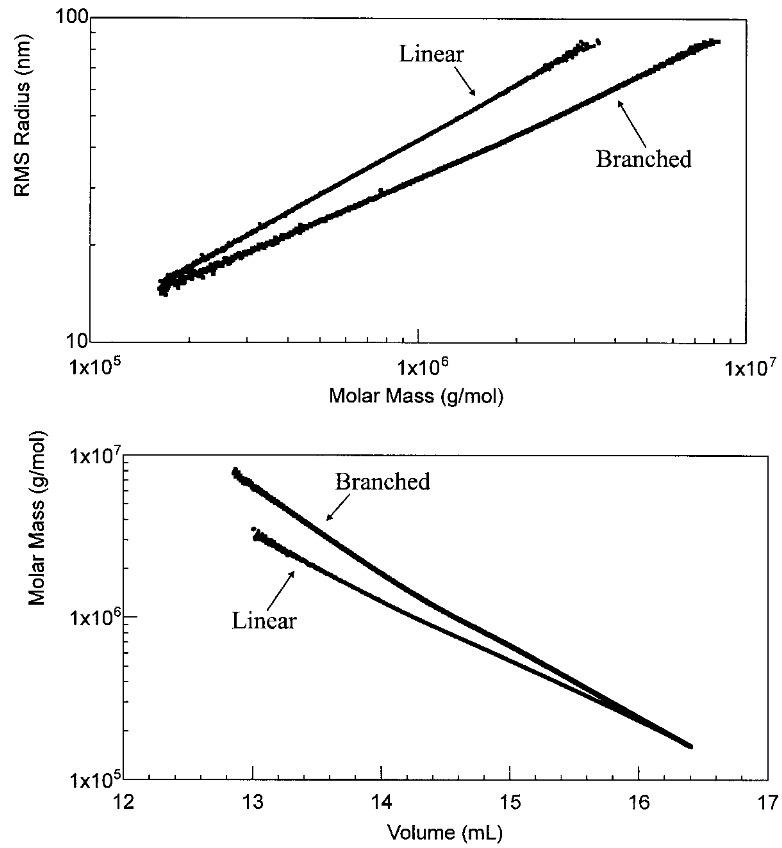

Figure 1 Conformation plots and molar mass versus elution volume plots for linear and randomly branched PS; slopes of conformation plots = 0.58 and 0.45.

= 0.0117 mL/g (PS),[20] a = 0.738, $K = 4.38 \times 10^{-3}$ mL/g (PBZMA, data obtained from [η] and M_w values of nine narrow fractions isolated by the precipitation fractionation of a broad sample). The RMS radii of linear polymers were calculated using the relations: $R = 0.014M^{0.585}$ (PS),[16] and $R = 0.0114M^{0.58}$ (PBZMA, data obtained from the RMS radius versus molar mass plot of a broad sample).

RESULTS AND DISCUSSION

Using the SEC-MALS method, information about the polymer chain conformation can be obtain from two plots:

1. RMS radius versus molar mass plot (conformation plot).
2. Molar mass versus elution volume plot.

Both plots relate the molar mass with a molecular dimension (expressed as either RMS radius or elution volume that corresponds to hydrodynamic volume). Examples of these plots for linear and randomly branched PS and linear and star-branched PBZMA are in Figures 1 and 2. Both examples show that at a given size (RMS radius or elution volume) the molar mass of branched polymer is higher than that of linear polymer.

The slope of the conformation plot permits linear and branched polymers to be distinguished. The typical values for linear random coils lie between 0.5 and 0.6, whereas lower values indicate the presence of branched molecules. For some branched samples, the increase of molar mass can be associated with little increase of RMS radius and the slope can be close to zero.

The determination of the conformation plot requires almost monodisperse volume slices. In general, the SEC separation of branched polymers is not so efficient as that of linear polymers because of the coelution of molecules of the same hydrodynamic volume, but different degree and architecture of branching. However, the experimental

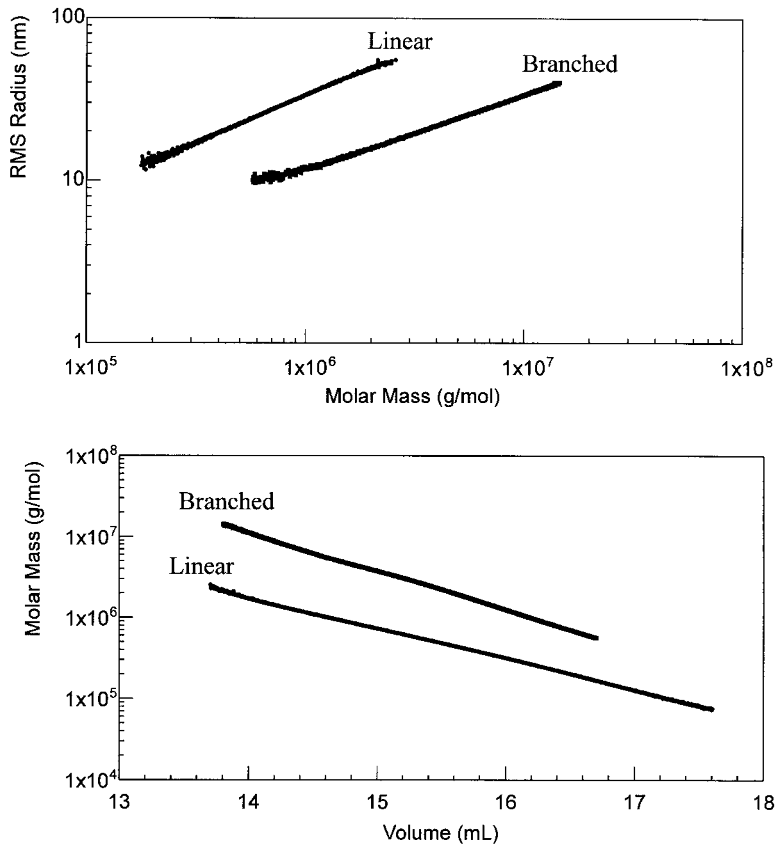

Figure 2 Conformation plots and molar mass versus elution volume plots for linear and star-branched PBZMA; slopes of conformation plots = 0.58 and 0.47.

results in Figures 1 and 2 prove that this separation is adequate.

Branching Ratio as a Function of Molar Mass

The relation between branching ratio and molar mass can be obtained by means of either the radius method or the mass method. The radius method compares the mean square radii at equal molar masses, whereas the mass method compares molar masses at equal elution volumes. Both methods require a plot of linear polymer overlapping the plot of branched polymer. The radius method employs eq. (1) and calculates the branching ratio directly without any theoretical or empirical assumptions. The mass method uses the following equation[21]:

$$g_M = \left(\frac{M_{lin}}{M_{br}}\right)_V^{(1+a)/e} \tag{5}$$

where M_{lin} and M_{br} are the molar masses of linear and branched polymer, respectively; a is the Mark–Houwink exponent for the linear polymer; and e is the draining parameter. The ratio of molar masses is taken at the same elution volume V and is calculated for all volume slices. Figures 3 and 4 compare the branching ratio versus molar mass plots calculated by means of the radius method and mass method using e = 0.5, 1, and 1.5. The comparison shows that the particular methods are not equivalent, and that the draining parameter e changes with molar mass. The value of draining parameter e around 1 can be recommended for the approximate estimation of branching ratio by the mass method.

Characterization of Branching in Case of Abnormal SEC Elution

The conformation plot and the relation between branching ratio and molar mass provide detailed description of a branched polymer. The data from SEC-MALS can be used for the calculation of number-, weight-, and z-average values of branching ratio. However, with increasing degree of branching

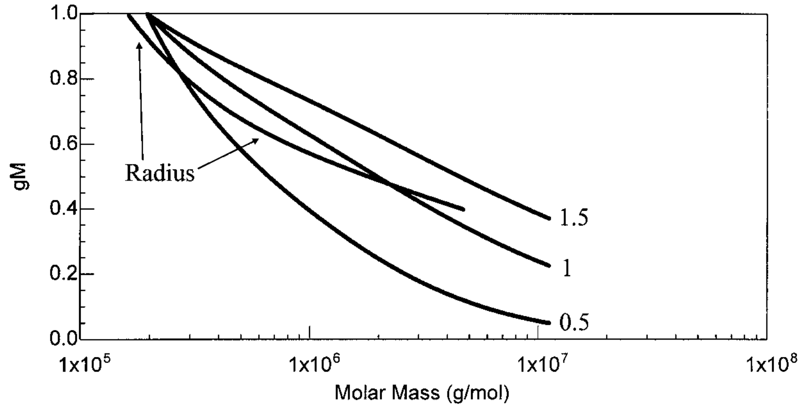

Figure 3 Branching ratio versus molar mass plots for randomly branched PS calculated by radius method and mass method using different values of *e* parameter.

there is increasing tendency to the abnormal SEC elution behavior that was investigated in the previous study.[22] Such elution behavior makes the determination of conformation plot impossible, and the branched samples have to be characterized by one of the following average parameters.

1. The average branching ratio g_M can be calculated from the experimental R_z of a branched polymer and the RMS radius of a linear polymer of the same z-average molar mass (M_z) as that of branched polymer. The calculation requires R_z and M_z of the branched polymer, and the relation RMS radius versus molar mass for the corresponding linear polymer. Both R_z and M_z can be obtained by SEC-MALS. The determination of R_z is not influenced by abnormal SEC elution because this quantity is determined by the first principle of light scattering. As shown previously,[22] good SEC separation can be obtained at least at the region of high molar masses. Consequently, good estimation of M_z (that is affected more by high molar mass fractions) can be obtained by SEC-MALS. This is the most appropriate method that uses solely the SEC-MALS data and does not require any additional information.
2. The average branching ratio g'_M can be calculated from the intrinsic viscosity of a branched polymer and the intrinsic viscosity of a linear polymer of the same M_w as that of branched polymer. The value of M_w can be determined by MALS either in SEC or batch mode, and the intrinsic viscosity can be simply measured by a capillary viscometer. The calculation of $[\eta]_{lin}$ requires constants K and a of the Mark–Houwink equation for the linear polymer.

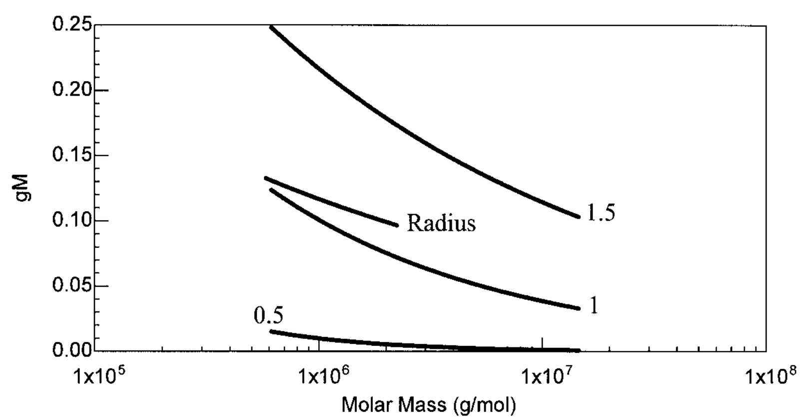

Figure 4 Branching ratio versus molar mass plots for star-branched PBZMA calculated by radius method and mass method using different values of *e* parameter.

Table I Values of M_w, g_M, g'_M, and M_w(SEC)/M_w for Randomly Branched PS Containing Different Amounts of DVB and Star-Branched PBZMA

Polymer	M_w (10^3 g/mol)	g_M	g'_M	M_w(SEC)/M_w
Linear PS	321	1.0	1.0	1.0
PS–0.20% DVB	183	0.72	0.80	0.92
PS–0.32% DVB	225	0.59	0.73	0.88
PS–0.39% DVB	263	0.58	0.64	0.85
PS–0.56% DVB[a]	371	0.43	0.59	0.77
PS–0.64% DVB	627	0.37	0.45	0.67
PS–0.73% DVB	1188	0.33	0.34	0.54
PS–0.83% DVB	1858	0.29	0.26	0.44
Linear PBZMA	399	1.0	1.0	0.64
Star-branched PBZMA	1024	0.10	0.17	0.22
Star-branched PBZMA[b]	2101	0.08	0.06	0.12

[a] The RMS radius versus molar mass, molar mass versus elution volume, and branching ratio versus molar mass plots for this sample are in Figures 1 and 3.

[b] The RMS radius versus molar mass, molar mass versus elution volume, and branching ratio versus molar mass plots for this sample are in Figures 2 and 4.

3. The ratio of weight-average molar mass determined by conventional SEC, M_w(SEC), to that determined by SEC-MALS can be used as another alternative. This approach has physical meaning, because M_w(SEC) is proportional to the average hydrodynamic volume. At constant M_w, the ratio M_w(SEC)/M_w decreases with increasing degree of branching. The ratio M_w(SEC)/M_w is related to SEC calibration obtained by PS standards, and therefore for various polymers it can be greater or less than 1. The ratio M_w(SEC)/M_w is the most empirical parameter that can be used only for the mutual comparison of samples of the same chemical composition. However, it may provide at least some branching information for samples for which the branching ratios g_M or g'_M cannot be determined.

Table I lists ratios g_M, g'_M, and M_w(SEC)/M_w for samples of different degree and structure of branching. The data in Table I show that all parameters decrease with increasing degree of branching, and enable distinguishing between less compact randomly branched molecules and more compact star-branched molecules. It is important to note that the branching ratio g_M cannot be calculated from g'_M, and vice versa, because they are determined on the basis of different molar mass averages.

CONCLUSIONS

The slope of the conformation plot can detect branching, even if the linear counterpart is unavailable. The branching ratio versus molar mass plot can be determined by either the radius method or the mass method. The radius method calculates branching ratio directly, as defined by Zimm and Stockmayer, without any theoretical or empirical assumptions. The calculation of the branching ratio by means of the mass method requires knowledge of the draining parameter e, which is generally unknown. The mass method can be useful mainly for lower molar mass polymers with RMS radii below about 10 nm.

Highly branched samples with abnormal SEC elution behavior can be characterized by average parameters g_M, g'_M, and M_w(SEC)/M_w, which can reveal the presence or absence of branching, allow sample comparison, and branching versus properties studies.

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