

Chapter 6

Characterization of Branched Polymers

6.1 INTRODUCTION

Branching of polymeric chains is one type of polymer nonuniformity. It is one of the most important molecular parameters that determines various physical, mechanical, and end-use properties of synthetic and natural polymers. Polymer properties affected by branching include glass transition temperature, mechanical properties (e.g., strength, tack, peel), viscoelastic properties, ability to crystallize, thermodynamic behavior (A_2 or θ -temperature), solubility, chemical resistance, phase separation of polymer mixtures, solution viscosity, melt viscosity, melt elasticity, rheological behavior of solutions and melts, workability, curing behavior of synthetic resins, and ability to swell. This last property can be of primary importance for drug delivery systems since the drug release rate can be controlled by the degree of branching of a polymer used as a drug carrier. Indeed, various branched polymers, such as branched polylactides, are of great interest for medical, biomedical, and pharmaceutical applications.

The effect of branching on polymer properties can be either negative or positive, depending on particular circumstances and polymer applications. For some properties the effect of branching may not be straightforward. For example, branching increases glass transition temperature (T_g) as a consequence of decreased mobility of polymer segments; on the other hand, increased concentration of chain ends increases free volume and thereby contributes to the decrease of the T_g . Similarly as for molar mass it may be necessary to find optimum values of branching, because positive effects on one property may result in negative effects on another property. The relation between type and degree of branching and polymer properties can be studied experimentally by means of model branched polymers or derived theoretically. Although it

may be difficult to predict properties of branched polymer unambiguously due to the variety of possible branching structures and the fact that many branching reactions occur in a random fashion, branching in polymers is undoubtedly an important structural variable that can be used to modify the processing and application properties of polymers. Some properties of specific branched polymers (e.g., dendrimers) are unachievable by means of linear polymers.

Some properties of branched polymers are very attractive. For example, branching is an efficient means of inhibition of polymer crystallization. That is because branching discourages the chains from fitting closely together so that the structure is amorphous with relatively large amounts of empty space, whereas structures with little or no branching allow the polymer chains to fit closely together, forming a crystalline structure. Another result of branching is that it reduces the molecular size. Consequently, branching is an effective way of reduction of solution viscosity. Some polymers may be easily melt-processable, but favorable processability may be associated with bad mechanical properties. Improvement in mechanical properties may cause processability to deteriorate, and branching of polymer chains may help to balance the two counteracting properties. The impact of branching on shear thinning (i.e., decrease of viscosity with increasing rate of shear stress) may play an important role in extrusion and injection molding. The impact on polymer dielectric properties may improve breakdown voltage and energy loss of capacitors. Various types of polyethylene play an important role as engineering polymers and thus the influence of long-chain branching on flow properties is of primary interest in the polyolefin industry. For instance, long-chain branches in polyethylene lead to significantly improved processing behavior due to increased shear thinning and strain hardening in elongation flow. An important fact is that even a very low level of branching can improve processing behavior in a sufficient manner.

One of the most important properties in rheology of polymer melts is the temperature dependence of the viscosity (Equation 1.89). The higher the activation energy E , the more temperature sensitive is the polymer melt. The value of E varies from polymer to polymer depending on chain composition. From a certain minimum value of molar mass (equal to the entanglement molar mass), E is independent on molar mass, but increases with the amount of long-chain branches. Branching is not only important from the viewpoint of structure–property and structure–property–processing relationships, but it brings valuable information about the polymerization mechanisms and extent and type of side reactions.

The term *degree of branching* refers to number of branch units in a macromolecule or number of arms in a starlike macromolecule. A *branched polymer* is a polymer containing at least one *branch unit* (branch point, junction point), that is, a small group of atoms from which more than two long chains emanate. A branch point from which f linear chains emanate is called an f -functional branch point. A distinguishing feature of branched polymers compared to linear polymers is presence of more than two chain ends. A branch is an oligomeric or polymeric offshoot from a macromolecular chain. An oligomeric branch is called

a *short-chain branch* while a polymeric branch is termed a *long-chain branch*. If the addition or removal of one or a few structural units has a negligible effect on the molecular properties, then the material can be considered to be a polymer and a branch can be considered to be a long-chain branch. Alternatively, if the branch length is comparable to the length of the backbone, the branched polymer can be termed as long-chain. However, the line between short-chain and long-chain is never explicit.

Branched molecules can be of varied structures, namely randomly branched molecules, combs, stars, dendrimers, and hyperbranched molecules. Even unusual branched structures such as centipedes or barbwire molecules have been reported in the literature. Branched molecules can arise as a result of various side reactions or can be prepared purposefully by simple or sophisticated synthetic pathways. Chain transfer to polymer, addition of water and glycols on double bonds during the synthesis of unsaturated polyesters, reaction of epoxy groups with aliphatic hydroxyl groups in epoxy resins, or polymerization of the second double bond in polyisoprene or polybutadiene are examples of side reactions leading to branching.

Free radical polymerization of a monovinyl monomer (e.g., styrene, acrylates, methacrylates) with the addition of a small amount of a divinyl monomerⁱ (e.g., divinyl benzene, ethyleneglycol dimethacrylate) represents the simplest example of the synthesis of branched polymers. The reaction technique is very straightforward and typically involves addition of free radical initiator to solution of monomers in a suitable solvent and polymerization at a temperature appropriate to the initiator. The resulting polymer has randomly (statistically) branched structure. At early stages of polymerization, predominantly only one of the vinyl groups of the divinyl monomer reacts and thus branch units appear at higher conversions. The length and number of branches can be partly controlled by the reaction temperature; varying the concentrations of divinyl monomer, initiator, and solvent; and using transfer agent.

Depending on the conversion and concentration of a polyfunctional monomer, the branching reaction can reach the gel point, that is, the stage when an infinitesimal fraction of indefinite structure appears in the system. At the gel point the weight-average molar mass reaches infinite value while the number-average molar mass is finite. With increasing reaction conversion after the gel point, the fraction of infinite insoluble structure (gel) increases while the amount of soluble fraction (sol) decreases and the M_w of sol decreases as well. A typical feature of a polymer prepared by free radical polymerization of a mixture of mono and divinyl monomers is a large fraction of linear molecules even at the proximity of gel point.

Another characteristic of randomly branched polymers is a presence of high-molar-mass tail and broadening of the molar mass distribution in comparison to the distribution that would arise under identical reaction conditions without

ⁱIn free radical polymerization, each vinyl group is difunctional (i.e., divinyl monomer is tetrafunctional).

presence of polyfunctional monomer. The probability that a randomly selected molecule will contain a branch unit increases with increasing molar mass and thus the degree of branching increases with increasing molar mass.

Randomly branched macromolecules can also arise by the radical polymerization of vinyl monomers due to the chain transfer to polymer. In contrast to the polymerization of monovinyl and divinyl monomer mixture, the resulting branch units are trifunctional. Another synthetic way to prepare randomly branched polymers is polycondensation of difunctional (e.g., hydroxy acid, mixture of dicarboxylic acids and glycols) and polyfunctional monomers (e.g., glycerol, pentaerythritol), which leads to polymers of equivalent structure to those prepared by radical polymerization with the exception of the presence of relatively high levels of oligomeric fractions even at high conversions. Other reactions leading to randomly branched polymers are heat treatment or irradiation of linear polymers. Branched macromolecules may be also formed during polymer aging.

Special synthetic methods can lead to branched polymers with well-defined structure compared to randomly branched polymers. Anionic polymerization is particularly suited for the preparation of branched polymers with controlled architecture. The technique yields polymers that retain their active chain ends even after all monomer has been consumed. These living polymers can react with multifunctional linking agents under formation of starlike polymers with the number of arms equivalent to the functionality of the linking agent. Possible heterogeneity is given by formation of stars containing different numbers of arms, as in the case of the reaction of poly(styryl)lithium with silicon tetrachloride, which usually leads to a mixture of three-arm and four-arm stars. Another synthetic way to form starlike polymers is living polymerization using multifunctional initiators.

Group transfer polymerization (GTP) is a technique applicable to the polymerization of methacrylic monomers, which in contrast to anionic polymerization yields living polymers at room temperature. The technique applies special initiators that enable synthesis of various polymethacrylates with controlled molecular structure. GTP synthesis of branched polymers involves two steps. Living arms from methacrylate are prepared in the first step, and then in the second step they react with a dimethacrylate monomer (e.g., ethyleneglycol dimethacrylate, EGDMA), which can react with up to four arms and partly also with itself. The resulting polymer consists of a dense EGDMA center from which numerous arms protrude. The method can provide starlike polymers with up to hundreds of arms and possibly functional groups located at the arm ends or in the arm chains. The properties can be further modified by the preparation of arms consisting of block copolymer.

Dendrimers are highly branched well-defined macromolecules with a branch point at each monomer unit, resembling the structure of trees. Their synthesis consists of numerous protection/deprotection and purification steps leading to products of increasing generation and molar mass. Dendrimers of higher generations of eight to ten reach the molar mass of several hundreds of thousands g/mol. Many interesting potential applications of dendrimers are based on their

molecular uniformity, highly dense structure, and multifunctional surface. On the other hand, the extreme laboriousness of their preparation, which requires multiple steps, is a serious limitation on their broader application.

Hyperbranched polymers represent a simpler alternative to dendrimers. They are prepared by a single-step polycondensation of AB_x ($x \geq 2$) monomers with different types of functional groups A and B capable of reacting with each other (e.g., dimethylol propionic acid, dimethylol butanoic acid). Hyperbranched polymers are expected to be highly branched like dendrimers; however, experimental results often indicate the presence of significant amounts of linear segments.

Macromonomers, that is, polymeric or oligomeric monomers with polymerizable functional groups at one end, can be used for the preparation of comb-shaped branched polymers with the distance between the branch units controllable with a regular low-molar-mass comonomer. In principle, macromonomers enable synthesis of polymers with a very high branch density.

6.2 DETECTION AND CHARACTERIZATION OF BRANCHING

In most branched polymers the distribution of degree of branching coexists with the distribution of molar mass and possibly with the distribution of other characteristics such as chemical composition. In addition, branched polymers are typical in variety of branching topology, as can be seen from the following simple example. Let us imagine a polymer molecule with two trifunctional branch units. The two branches can protrude from the backbone or one branch can protrude from the other, and they can have various positions with respect to the chain ends. If the branches are located close to the backbone ends, then the entire molecule virtually behaves as a linear molecule. This simple example shows that a branched molecule of a given molar mass and branching degree can occur in numerous positional isomers.

Another reaction complicating the architecture of branched polymers is the possible formation of intramolecular rings due to the reaction that occurs between two segments of the same macromolecule. Branched polymers mostly consist of molecules of different molar mass and degree of branching, which is particularly true in the case of randomly branched polymers. Molecules of identical molar mass can differ in the number of branch units, and macromolecules of identical molar mass and number of branch units can differ in the position of branch units in a polymer chain.

Thorough characterization of branched polymers involves not only the determination of the distribution of molar mass, but also the distribution of branching degree. However, there is no experimental technique that would enable separation of polymer molecules purely according to the degree of branching and regardless of their molar mass. The temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF) techniques utilize the different crystallizability brought in by short-chain and long-chain branches to fractionate

polymer on the basis of the branching degree. In principle, this mechanism permits characterization of the branching distribution, but the applicability of both methods is limited mainly for the analysis of polyethylene and polyethylene-based copolymers. In addition, although the separation is expected to be according to the degree of branching, there is also simultaneous separation on the basis of molar mass. In a conventional arrangement with a concentration detector only (infrared detector) there is no information about the molar mass of fractions eluting from the TREF/CRYSTAF system, and the obtained fractions must be further characterized.

Another method attempting the separation of molecules according to their branching degree has been reported by Meunier et al.¹ The method is based on the idea of anchoring of branched molecules in porous matrix, described in reference 2. It uses monolithic columns to create a tortuous path where the flow-through channels have size of the order of polymer molecular dimensions. Because the long-chain branched molecules are retained more than linear molecules of the same size, the method can be used to separate branched chains from linear molecules. The method may succeed in separating simple branched polymers, such as mixtures consisting of four-arm and three-arm stars and residual linear molecules. However, it is unlikely that the method would allow efficient separation of complex branched polymers solely according to the branching degree.

Two-dimensional chromatography may offer another possible approach in the more detailed characterization of various branched polymers, where fractions of identical hydrodynamic volume obtained by SEC in the first step can be further separated according to the branching degree by a suitable type of interaction chromatography in the second step.

Currently, the only really measurable branching distribution is the degree of branching as a function of molar mass. In fact, the branching ratio determined at a given molar mass is an average for all molecules having this molar mass, because the molecules may have different degrees of branching at the same molar mass. That means molecules of a given molar mass consist of molecules with a certain distribution of branching degree. Another complicating fact is that the available analytical separation techniques separate on the basis of hydrodynamic volume and not molar mass. Consequently, the molecules eluting from the separation system at a given elution time have the same hydrodynamic volume, but different degrees and topologies of branching and also different molar masses. In a rigorous manner the obtained result is the relation between the average branching degree (average for a given average molar mass) and the average molar mass (average for a given hydrodynamic volume).

Various methods providing relationships between branching degree and molar mass will be described in this chapter. Taking into account the complexity of branched polymers with respect to their molar mass distribution, number of branch units per molecule, and branching topology, a detailed description of branching is virtually impossible. In reality, detection of the presence of branched molecules and estimation of the degree of branching as a function of molar mass

and the determination of an average branching characteristic for the entire sample is the only obtainable information for most branched polymers.

The characterization of branching is often complicated by the impossibility of preparing well-defined branched model polymers. Although sophisticated synthetic routes can yield well-defined stars or combs, the preparation of well-defined models for randomly branched polymers is impossible. For some polymers even the preparation of a linear counterpart of identical chemical composition is impossible, as in the case of various synthetic resins (e.g., alkyds, phenol-formaldehyde resins, epoxies). Also the tendency of various acrylates (not methacrylates) to chain transfer to polymer is so strong that it may be difficult to prepare purely linear homopolymers by free radical polymerization.

It may be noted that structure and number of branches in a polymer sample can be revealed from the rheological measurements.^{3,4} Rheological experiments conducted on irradiated polypropylene were shown⁴ to be more sensitive with respect to long-chain branching than characterization by means of SEC-MALS. However, rheological measurements are not applicable to all kinds of branched polymers and the obtained results are merely average characteristics with no information about branching distribution. Although the presence of branch units can be in principle detected by spectral techniques, the level of long-chain branching is often that low that it cannot be detected by standard analytical methods. Branched molecules can be detected and characterized indirectly by the measurement of dilute solution properties. A review of solution properties of branched macromolecules can be found in reference 5.

The fundamental principle of detection and characterization of branching is based on the fact that at a given molar mass the molecular size decreases with increasing degree of branching. In other words, branching reduces the molecular size and increases the compactness of the macromolecules. This means that to get branching information it is necessary to determine both molar mass and molecular size. The analytical methods commonly applicable for the investigation of branching can be divided into two categories: (1) characterization methods, mainly light scattering, dynamic light scattering, and viscometry, and (2) separation methods, mainly SEC and field flow fractionation techniques. The characterization methods can be used in batch mode or in combination with a separation technique.

A numerical description of the degree of branching can be achieved by the parameter defined by Zimm and Stockmayer:⁶

$$g = \left(\frac{R_{br}^2}{R_{lin}^2} \right)_M \quad (6.1)$$

where R^2 is the mean square radius of a branched (*br*) and a linear (*lin*) macromolecule of the same molar mass (M). The parameter g is called *branching ratio* (*branching index*, *branching parameter*, or *contraction factor*) and is equal to unity for linear polymers and decreases with increasing extent of branching. For polymers with a very high degree of branching, the ratio g approaches values around 0.1, but never zero. It is also evident from the definition of g that it is never larger than 1.

Branching frequency (λ), defined as the number of branch units per 1,000 repeat units, is another parameter that can be used for the description of branched polymers and is frequently used in the analysis of polyolefins. Branching ratio itself can serve for the characterization of branching degree, and it can be used for further calculations. As shown by Zimm and Stockmayer, the branching ratio g allows calculation of number of branch units per molecule or number of arms in starlike molecules. Various theoretical equations describing the structure of branched polymers can be found in the literature.⁶⁻¹¹ The most frequently stated relations are those derived by Zimm and Stockmayer for randomly branched and star-branched polymers.⁶

For randomly branched polymers with tri- or tetrafunctional branch units, the ratio g is given by the equations:

$$g_3 = \left[\left(1 + \frac{m}{7} \right)^{\frac{1}{2}} + \frac{4m}{9\pi} \right]^{-\frac{1}{2}} \quad (6.2)$$

$$g_4 = \left[\left(1 + \frac{m}{6} \right)^{\frac{1}{2}} + \frac{4m}{3\pi} \right]^{-\frac{1}{2}} \quad (6.3)$$

where m is the average number of branch units per molecule and subscripts 3 and 4 refer to trifunctional and tetrafunctional branch units. For instance, the polymerization of vinyl monomers with an addition of a small amount of a divinyl monomer results in tetrafunctional branch units while chain transfer to polymer creates trifunctional branch units. In a given example, both functionalities can occur simultaneously, the former being relatively easily controllable by the amount of divinyl monomer and conversion, the latter being indirectly controllable by reaction conditions. Simultaneous existence of branch units of different functionality may be also expected in the case of polyfunctional monomers, for instance in polycondensation of a mixture of difunctional monomers with addition of a tetrafunctional monomer, which can undergo reaction completely, giving tetrafunctional branch units, or incompletely, giving trifunctional branch units. Trifunctional randomly branched topology can be assumed in branched polymers formed by irradiation, because formation of branch points with higher functionality is statistically improbable.

Equations 6.2 and 6.3 were derived for the case where a material of heterogeneous molar mass containing randomly distributed branch units is fractionated into a series of samples, each of them being monodisperse but of different molar mass, and the branch units in each fraction are still randomly distributed. As a matter of fact, these conditions approximately correspond to the situation occurring in SEC or FFF. Since m is the average number of branch units (actually the number-average), the ratio g given by Equations 6.2 and 6.3 is the average value valid for molecules of the same molar mass but different numbers of branch units.

The expressions for polymers heterogeneous with respect to molar mass are:

$$g_{3,w} = \frac{6}{n_w} \left[\frac{1}{2} \left(\frac{2 + n_w}{n_w} \right)^{\frac{1}{2}} \ln \left(\frac{(2 + n_w)^{\frac{1}{2}} + n_w^{\frac{1}{2}}}{(2 + n_w)^{\frac{1}{2}} - n_w^{\frac{1}{2}}} \right) - 1 \right] \quad (6.4)$$

and

$$g_{4,w} = \frac{\ln(1 + n_w)}{n_w} \quad (6.5)$$

where n_w is the weight-average number of branch units per molecule and the subscripts indicate functionality of the branch unit and the fact that the ratios are the weight-averages.

For the z -average values of g , the formulas derived in reference 6 are:

$$g_{3,z} = \frac{1}{1 + \frac{n_w}{3}} \quad (6.6)$$

and

$$g_{4,z} = \frac{1}{1 + n_w} \quad (6.7)$$

For stars with f arms of random length, the branching ratio is given by the equation:⁶

$$g = \frac{6f}{(f + 1)(f + 2)} \quad (6.8)$$

And for regular stars with arms of equal length:

$$g = \frac{3f - 2}{f^2} \quad (6.9)$$

Note that for the linear molecules, $f = 2$ or $m = 0$, the above formulas yield the value unity. The graphical representation of Equations 6.2, 6.3, and 6.8 is shown in Figure 6.1.

It must be emphasized that the above equations were derived assuming unperturbed chain statistics for both linear and branched macromolecules, that is, assuming no excluded volume effect. However, the real measurements are mostly carried out in thermodynamically good solvents where the molecules expand due to intensive interactions between polymer molecules and solvent. The expansion of a polymer chain is more pronounced in the case of linear molecules, and thus the ratio g determined in thermodynamically good solvent is smaller than it would be in theta solvent and the branching degree is overestimated. The correction for the excluded volume effect yields equations that are complicated, with several parameters generally unknown or at least uncertain. In reality, the effect of the excluded volume is probably lower than experimental and other uncertainties and thus can be neglected. The selection of an appropriate equation relating g with a parameter characteristic for a given branched structure may not

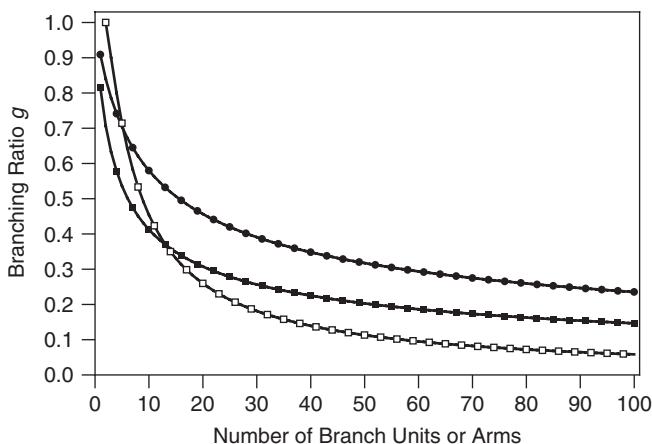


Figure 6.1 Branching ratio as a function of number of branch units per molecule for three (●) and four (■) functional branch units in randomly branched polymer and number of arms (□) in star-branched polymer (Equations 6.2, 6.3, and 6.8).

be always straightforward, because the functionality of branch unit or the type of branched structure may not be known. In addition, the theoretical equations were typically not verified by experiments due to lack of well-defined branched standards.

Although the application of theoretical equations may not provide an absolutely accurate description of a branched polymer, especially when the measurement is carried out far from θ -conditions, the equations can yield an estimate of m or f , mutual comparison of various samples with respect to their branching degree, and indicate the effectiveness of synthetic techniques with respect to their ability to yield branched polymers of desired structure. The equations relating g with the number of branch units or arms are only one part of branching characterization; before they can be applied, a reliable value of g must be determined by a suitable experimental technique. The main objective of this chapter is to show the most important methods available for the characterization of branching and discuss their advantages and limitations. The focus is on methods that have general applicability and that are relatively easy to apply.

As described in Chapter 2, the molar mass and the root mean square radius, which are necessary to characterize branched molecules by parameter g , can be obtained by multi-angle light scattering. One serious limitation of MALS is that when applied on unfractionated polymer sample it yields M and R of different moments, namely the weight-average molar mass and the z -average RMS radius. The two averages are of different sensitivities to high-molar-mass species; consequently, batch MALS usually can provide branching information only for monodisperse or very narrow polymers. Combination of MALS with a separation method overcomes this limitation to a great extent since M and R are measured for narrow fractions eluting from the separation device.

Traditional methods of polymer fractionation, such as precipitation fractionation, are of limited applicability due to their laboriousness and low efficiency with respect to the polydispersity of obtained fractions. SEC and A4F, or other FFF techniques, are separation methods that can be used in combination with MALS for the characterization of branched polymers. However, in comparison to linear polymers, where the local slice polydispersity is given solely by the band broadening in the SEC columns or A4F channel and can be reduced by optimization of separation conditions, branching represents another contribution to the polydispersity of fractions eluting from an SEC or AF4 system. Since both methods separate molecules according to their hydrodynamic volume, in a given elution volume all molecules eluting from the separation device have identical hydrodynamic volume (assuming absence of band broadening), but different molar masses, numbers of branch units, and chain architectures. Consequently, a MALS detector does not measure the molar mass and RMS radius, but their averages. Nevertheless, as there is no simple method providing information about the polydispersity of fractions eluting from SEC columns or A4F channel, the polydispersity effect must be neglected and the molar masses and RMS radii must be treated as if they were determined for monodisperse fractions. This is a basic assumption that one has to accept at least for routine characterization.

Characterization of branching on the basis of RMS radius is also limited by the fact that RMS radius cannot be determined for smaller polymer molecules with RMS radii below about 10 nm, which roughly corresponds to molar mass of 10^5 g/mol. That means the size of many branched polymers cannot be determined by elastic light scattering. There are two alternative techniques that can be used for the determination of size below 10 nm: dynamic light scattering and viscometry of dilute solutions. The latter one is especially efficient for the determination of size of polymer molecules covering broad molar mass range. The intrinsic viscosity, $[\eta]$, describes the size of polymer molecules in a dilute solution. An alternative branching ratio was defined as the ratio of the intrinsic viscosities of a branched (*br*) and a linear (*lin*) macromolecule of identical molar mass:¹²

$$g' = \left(\frac{[\eta]_{br}}{[\eta]_{lin}} \right)_M \quad (6.10)$$

The mutual relationship of the two branching ratios can be expressed by a simple relation:

$$g' = g^e \quad (6.11)$$

where e is a parameter related to drainability of a polymer chain, the values of which are usually assumed to vary from 0.5 to 1.5. The value of e depends on solvent, molar mass, temperature, and branching. An important advantage of intrinsic viscosity is that it can be accurately determined even for small polymer molecules with molar masses down to about a thousand g/mol with practically no upper limit. In contrast to RMS radius, the weight-average intrinsic viscosity, $[\eta]_w$, is measured for an unfractionated sample and therefore the combination of MALS with a capillary viscometer can be used for the determination of average

g' by batch measurements. However, considerably more information can be obtained by means of an online viscometer combined with an SEC-MALS setup.

6.2.1 SEC Elution Behavior of Branched Polymers

As already mentioned, the polydispersity of elution volume slices in SEC separation of branched polymers is generally larger compared to linear polymers separated under the same separation conditions because of co-elution of molecules of the same hydrodynamic volume, but different molar masses and branching. However, for many branched polymers there is an additional, substantially more serious contribution that increases the local polydispersity within the elution volume slices. Many branched polymers show the SEC elution that is demonstrated in Figure 6.2, which depicts plots of molar mass and RMS radius versus elution volume for a randomly branched polymer. At lower elution volumes both molar mass and RMS radius decrease evenly with increasing elution volume, as is typical of SEC separation. At a certain point in the chromatogram both quantities

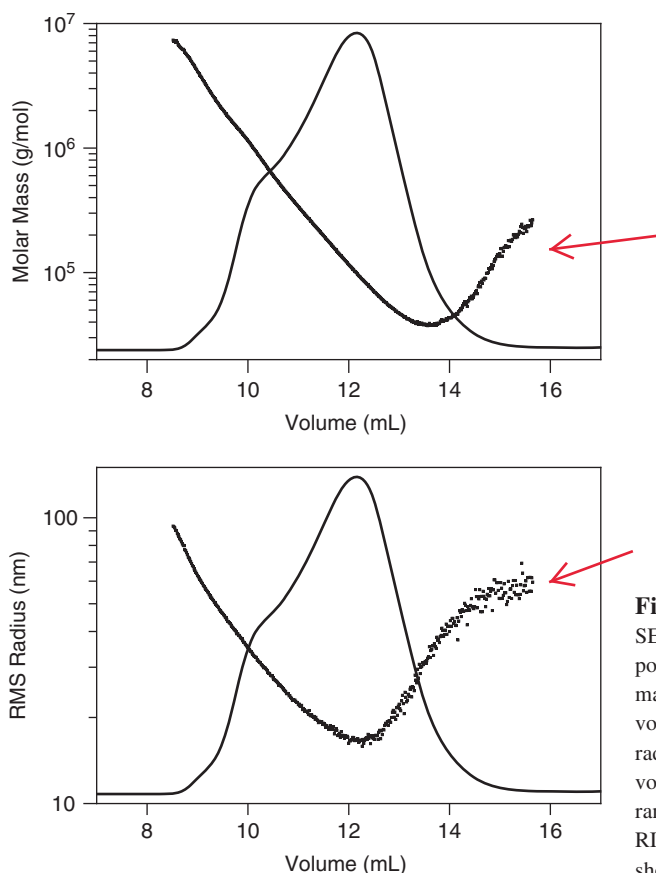


Figure 6.2 Abnormal SEC elution of branched polymer: Molar mass-versus-elution volume (top) and RMS radius-versus-elution volume (bottom) plots of randomly branched polymer. RI chromatogram is also shown here.

start to increase with increasing volume. For the RMS radius this **upturn** appears at a lower elution volume than for the molar mass. Although this SEC elution behavior is not observed for all branched polymers, **it is frequent and becomes more pronounced with increasing degree of branching.**

This behavior was reported by several authors and explained in different ways. It was systematically studied in reference 2, where the influence of various experimental parameters (e.g., flow rate, column type, temperature) on the pattern of molar mass and RMS radius plots was investigated. The most important finding was that the abnormal elution behavior was **not found in the separation by thermal FFF**, which was afterward repeatedly verified by separation using A4F, as shown later in this chapter.

On the basis of the obtained results, the abnormal SEC elution was explained by **the entanglement of large, highly branched molecules in the pores of column packing.** Since the previously used term *entanglement* is also used with respect to the concentration at which the polymer chains in solution start to overlap, the term *anchoring* will be used in this book to avoid confusion of the two phenomena. **Anchoring is where particular parts of large branched molecules can behave as separate molecules, penetrate into the pores, and anchor the entire molecules.**

This anchoring idea is sketched in Figure 6.3. Due to the anchoring effect **some large molecules are delayed and elute at higher elution volumes than would correspond to their hydrodynamic volumes.** The fractions eluting from SEC columns at the region of high elution volumes consist of smaller molecules separated by a purely SEC mechanism and very large branched molecules that were delayed by the anchoring effect. In such a case, the assumption of monodisperse fractions eluting from the SEC columns is not valid, the local polydispersity cannot be neglected, and the MALS detector yields values of M_w and R_z instead of values of M and R . The R_z is more sensitive to the presence of small amounts of fractions with very high molar mass than the M_w , and thus the upswing on the RMS plot appears at a lower elution volume compared to the molar mass. Simple estimation leads to the conclusion that the concentration of contaminating large molecules is rather low. For example, taking data from Figure 6.2 it is possible to estimate that the fractions of smaller macromolecules eluting at about

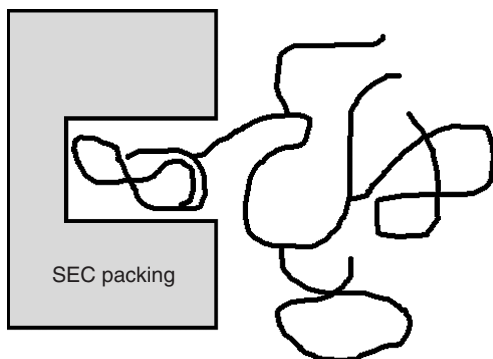


Figure 6.3 Illustration of the anchoring of a large branched molecule in a pore of column packing by a part of the polymer chain.

15 mL have molar mass around 10,000 g/mol. This number can be obtained by extrapolation of a molar mass–versus–elution volume plot from the region of low elution volumes to the high elution volumes. The molar mass measured by the MALS detector at this elution volume is about 140,000 g/mol. Assuming that the delayed molecules are of molar mass of the order of magnitude of 5×10^6 g/mol, that is, approximately the molar mass measured at the beginning of the chromatogram, one can estimate the fraction of the delayed molecules as follows:

$$140,000 = w_1 \times 10,000 + (1 - w_1) \times 5 \times 10^6$$

where w_1 is the weight fraction of molecules with molar mass 10,000 g/mol and $(1 - w_1) = w_2$ is the weight fraction of molecules with molar mass 5×10^6 g/mol. For this particular example, we get $w_2 = 0.026$; that is, delayed macromolecules represent approximately 2.6% of eluting molecules. The reality is certainly more complicated; co-eluting macromolecules are of different molar mass and the upturn on the molar mass and RMS radius plots can be caused by a trace level of ultra-high-molar-mass, highly branched fractions. For some highly branched polymers the anchoring effect is so strong that the light scattering signal tails to the elution volumes beyond the limit of total permeation of SEC columns. That means the molecules are delayed by anchoring for a relatively long time and they elute at very low concentrations detectable only by a light scattering detector.

An unwelcome consequence of the anchoring effect is **the upswing on the conformation plot**, as shown in Figure 6.4. It must be emphasized that the upswing on the conformation plot from SEC-MALS is **totally virtual**; that is, there are no molecules in the analyzed sample that would have two different radii at the same molar mass as one can see at the lower-molar-mass part of the conformation plot in Figure 6.4. **The upswing is caused by the nonnegligible polydispersity of the fractions eluting at the end of the chromatogram and the higher sensitivity of R_z to the polydispersity compared to M_w .**

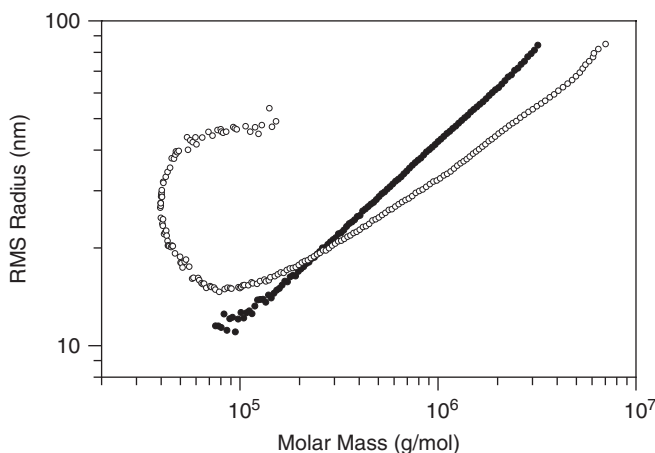


Figure 6.4 Conformation plots for linear (●) and randomly branched (○) polystyrene determined by SEC-MALS. The same polymer as in Figure 6.2.

6.2.2 Distribution of Branching

Branching distribution is usually characterized by the relation between the branching ratio and molar mass and consequently the relation between the number of branch units and molar mass. As already explained, this is usually the only measurable branching distribution, because the available separation techniques separate according to hydrodynamic volume and there is no generally working separation technique separating primarily on the basis of branching degree. The acquisition of requested experimental data requires hyphenation of an analytical separation technique and characterization methods capable of providing molar mass and molecular size. The characterization of branching distribution is based on the assumption of almost monodisperse fractions eluting from a separation system. That means an efficient separation analytical technique is crucial for accurate branching characterization.

Although the separation of branched polymers is generally less efficient than the separation of corresponding linear polymers, the experimental results for many branched polymers suggest that SEC and especially A4F are usually sufficient to provide useful branching information. For routine characterization of branched polymers, the slice polydispersity is neglected and the effort is focused on optimization of separation conditions, especially in the sense of minimizing the undesirable anchoring effect. Generally, there are three methods that can be used for determination of ratio g as a function of molar mass: (1) *radius method* (calculation of g from R at the same M), (2) *mass method* (calculation of g from M at the same elution volume), and (3) *viscosity method* (calculation of g' from $[\eta]$ at the same molar mass).

Figures 6.4–6.6 show typical results obtained by SEC-MALS or SEC-MALS-VIS analysis of a branched polymer and a corresponding linear counterpart. They are: (1) RMS radius–versus–molar mass plot (radius method

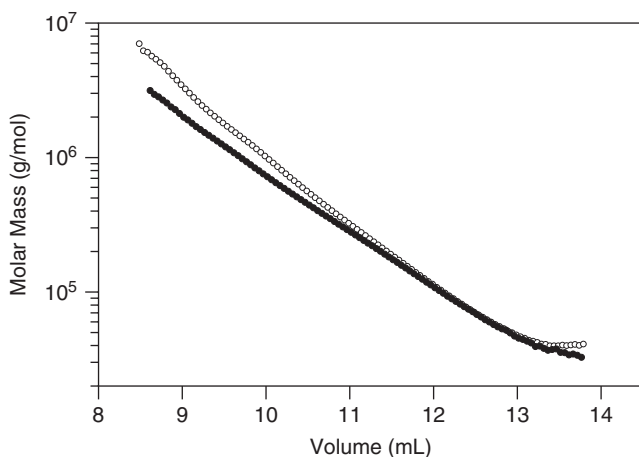


Figure 6.5 Molar mass–versus–elution volume plots for linear (●) and randomly branched (○) polystyrene (conformation plots are in Figure 6.4).

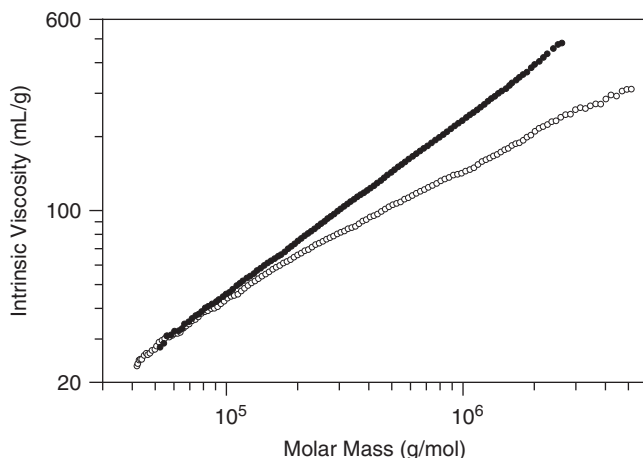


Figure 6.6 Mark-Houwink plots for linear (●) and randomly branched (○) polystyrene (conformation plots are in Figure 6.4).

of calculation of g), (2) molar mass–versus–elution volume plot (mass method), and (3) Mark-Houwink plot (viscosity method). All three plots relate the size information with the molar mass. The first two plots can be obtained using only SEC-MALS; the determination of the Mark-Houwink plot requires coupling the SEC-MALS instrument with an online viscometer.

The relation between the RMS radius and molar mass (*conformation plot*) is one of the basic tools for detection and characterization of branching. The conformation plots of linear polymers in thermodynamically good solvents are linear with the slopes around 0.58. In the case of branched polymers the slope of the conformation plot decreases with increasing degree of branching. Some conformation plots show leveling off toward high molar masses. The conformation plot can prove the presence or absence of branching even if the linear counterpart is unavailable. However, the decrease of the slope at low branching degrees is small (for example, from 0.58 to 0.55), which makes the detection of branching without a linear counterpart uncertain.

The slope of the conformation plot can be also influenced by the light scattering formalisms used for data processing (see Section 4.3.4) and possibly also by the separation range of the SEC columns. If the sample contains molecules with molar mass over the exclusion limit of the SEC columns, these molecules elute nonseparated at the beginning of the chromatogram and the MALS detector measures for that region M_w and R_z , which may result in the increase of the slope of the conformation plot. In such a case, the data from the beginning of the chromatogram should not be used for the determination of the slope; the same is true for the data points at the end of the chromatogram, which are often scattered due to the low concentration and molar mass of eluting molecules.

As already discussed, the conformation plots from SEC-MALS of many branched polymers show a noticeable upswing at the region of lower molar

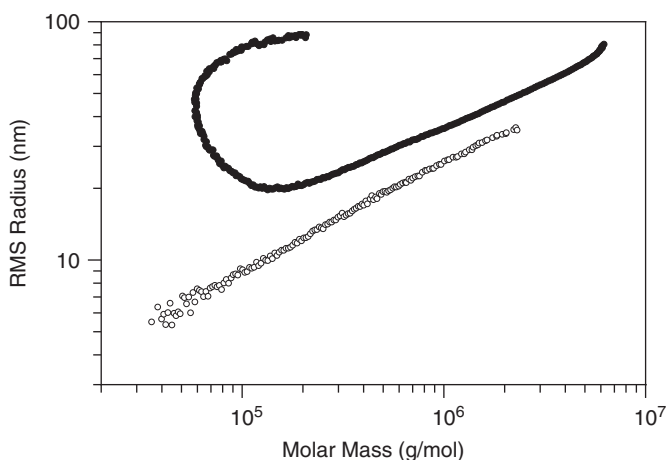


Figure 6.7 Conformation plots of two different branched samples with and without upswing. M_w , g_{M_z} and g'_{M_w} are listed in Table 6.1 for PS B2 (●) and PS 20 (○).

masses. In fact, the upswing is so typical that it may serve as evidence of the presence of branching. It has been explained that the upswing is a consequence of the anchoring of branched macromolecules in the pores of column packing during their flow through the SEC columns.

Although the upswing on the conformation plot is quite frequent, it may be missing on the conformation plots of some branched polymers as shown in Figure 6.7. The upswing is negligible especially in the case of polymers with lower degree of branching, branched samples that do not contain molecules with very high molar masses or polymers with relatively short branches. This is because smaller branched molecules or molecules with relatively short branches cannot be anchored in the way shown in Figure 6.3. The upswing also becomes less pronounced with decreasing sample polydispersity.

The intensity of the upswing is also related to the type of SEC columns used for the separation, as demonstrated in Figure 6.8, which shows that the upswing is more pronounced when SEC columns with smaller particle size and smaller pore size are used for the SEC separation. The upswing can be also partly eliminated using very low flow rates such as 0.1 mL/min. However, working at such low flow rates increases run time and the change in the flow rate typically results in increased noise level of a MALS detector due to release of particles from SEC columns. Stabilization of the signal at a very low flow rate takes a long time, and thus working at extremely low flow rates appears impractical. The only effective solution to the anchoring problem is change of the separation technique.

The upswing is completely eliminated when A4F is applied instead of SEC, as shown in Figure 6.9. The comparison of SEC-MALS and A4F-MALS results for various branched polymers proved unambiguously A4F to be a more efficient separation technique for branched polymers. This is certainly true mainly for

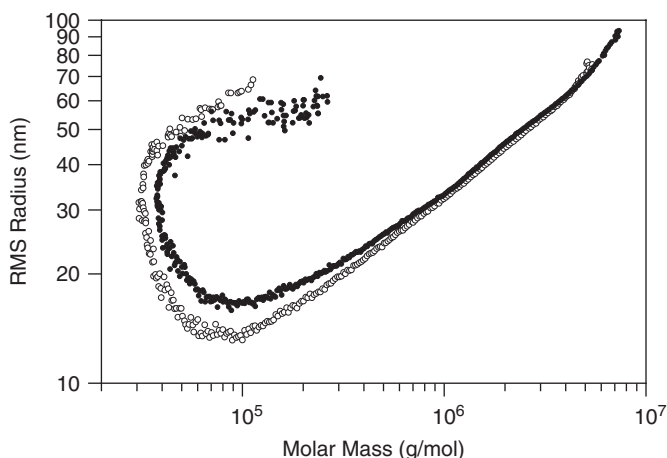


Figure 6.8 Conformation plots of randomly branched PS obtained by two different columns: $2 \times$ Plgel Mixed-C (●) and $2 \times$ Plgel Mixed-B (○). Mixed-C is $5\text{-}\mu\text{m}$ particle size column packing with operating range $200\text{--}2 \times 10^6$ g/mol; Mixed-B is $10\text{-}\mu\text{m}$ packing with operating range $500\text{--}10^7$ g/mol.

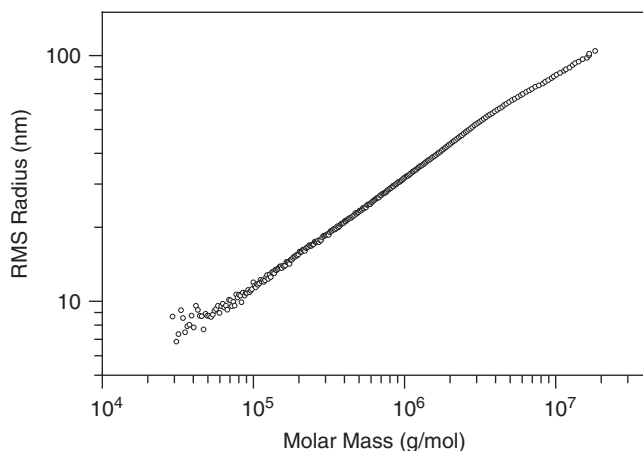


Figure 6.9 Conformation plot of branched polystyrene determined by A4F-MALS. (For comparison with SEC-MALS, see Figure 6.4).

large polymers with a tendency to anchor in the SEC column packing, whereas for smaller molecules SEC usually provides satisfactory results.

SEC elution volume is related to molecular size and therefore the relation between the molar mass and elution volume can be used for branching studies. Using the approach of Yu and Rollings,¹³ the molar mass–versus–elution volume plots of a branched polymer and a linear polymer of the same chemical composition measured under identical separation conditions can yield the branching

ratio according to the equation:

$$g = \left(\frac{M_{lin}}{M_{br}} \right)_V^{\frac{1+a}{e}} \quad (6.12)$$

where M is the molar mass of linear (*lin*) and branched (*br*) molecules eluting at the same elution volume V , a is the exponent of the Mark-Houwink equation of a linear polymer in a given solvent and at a given temperature, and e is the draining parameter.

Calculation of g from the molar mass-versus-elution volume plots appears to be the least appropriate method of branching characterization, because it strongly depends on separation conditions and has no general validity. It requires knowledge of two parameters, a and e , which may not be always known. On the other hand, the molar mass-versus-elution volume plot is applicable over a broad molar mass range including oligomers. The molar mass-versus-elution volume plots can be valuable for mutual graphical comparison of samples measured under identical separation conditions. The mass method does not require the measurement of RMS radius, which makes it less sensitive to anchoring phenomena. Since the molecular size is not measured directly, but merely estimated from the elution volume, the method is highly sensitive to any kind of non-SEC separation.

In contrast to the molar mass-versus-elution volume plot, the conformation plot and the Mark-Houwink plot relate absolute quantities obtained by MALS and VIS detectors. They do not require concurrent measurement of a linear counterpart, but previously established relationships R versus M or $[\eta]$ versus M for a corresponding linear polymer can be used for branching detection and characterization.

An important finding is the significantly lower sensitivity of the Mark-Houwink plot to the anchoring effect. The explanation is that in the case of poor SEC separation the conformation plot relates R_z with M_w , whereas the Mark-Houwink plot relates $[\eta]_w$ with M_w , and thus the effect of poor separation is at least partly eliminated because both quantities are equally affected by increased polydispersity.

Figure 6.10 compares branching ratios g and g' obtained from the data depicted in Figure 6.4 and Figure 6.6. Branching ratio g' starts at about unity and decreases with increasing molar mass. This is typical behavior for randomly branched polymers, because the probability that a randomly selected macromolecule contains a branch unit increases with increasing polymerization degree. Consequently, in randomly branched polymers the fractions with lower molar mass are mostly linear while the fractions with higher molar mass are more branched. The branching ratio g calculated from the RMS radius shows different behavior. At the region of high molar masses it goes approximately parallel with g' , while at the region of lower molar masses it goes for above unity, which is a maximum value of this parameter. As already explained, this is caused by increased polydispersity of fractions eluting at the region of higher elution volumes.

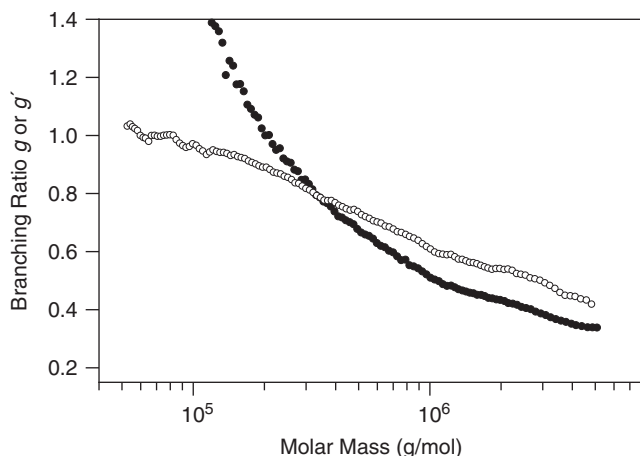


Figure 6.10 Molar mass dependence of branching ratios g (●) and g' (○) calculated using the data from Figures 6.4 and 6.6.

To avoid misunderstanding, it must be stressed that g of branched polymers is always smaller than unity if the branched and linear molecules are compared at the same molar mass or at the same molar mass moment. It has been shown in reference 14 that g of a branched polymer can be larger than unity in the case of an unfractionated sample when the RMS radii are compared at the same M_w , which is exactly the case in SEC-MALS when some elution slices are polydisperse due to the anchoring effect.

Figure 6.11 contrasts the parameter g -versus-molar mass plots determined by A4F-MALS and by SEC-MALS. The two plots overlap at the region of

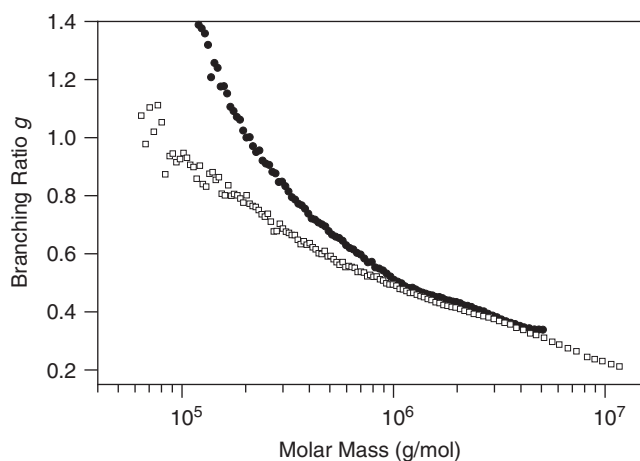


Figure 6.11 Branching ratio g -versus-molar mass plots of randomly branched polystyrene determined by SEC-MALS (●) and A4F-MALS (□).

high molar masses, where the anchoring effect in SEC is imperceptible and elution slices are narrow, and deviate toward lower molar masses due to the rising polydispersity of the SEC slices. The contamination with large branched molecules decreases toward lower elution volumes and obviously there is no contamination at the very beginning of the chromatogram. It may be noted that the anchoring affects not only the ability of SEC-MALS to characterize branching, but also the ability to determine the molar mass distribution and molar mass averages. Since light scattering measures M_w and R_z by its first principle, these two quantities are correct even in the case of poor SEC separation. On the other hand, the value of M_n is affected strongly, because the lower-molar-mass fractions are the most contaminated. As the contamination effect is small at the beginning of the chromatogram, the value of M_z that counts strongly the high-molar-mass fractions can be considered to be almost correct (assuming no shearing degradation).

The distribution of branching along the molar mass axis (i.e., plots of g versus M or m versus M) can be overlaid with the molar mass distribution curve as shown in Figure 6.12. Such a plot permits the determination of branching distribution with respect to the molar mass. Using the data presented in Figure 6.12 one can see that molecules with molar mass below about 10^5 g/mol are linear. This represents almost 40% of molecules in the given sample. The fraction of molecules with molar mass over 10^6 g/mol represents about 8%, which means about 8% of molecules in the sample have more than seven branch units on average.

Figure 6.13 compares branching results obtained by means of radius and viscosity methods. It shows the relation between g obtained directly from the

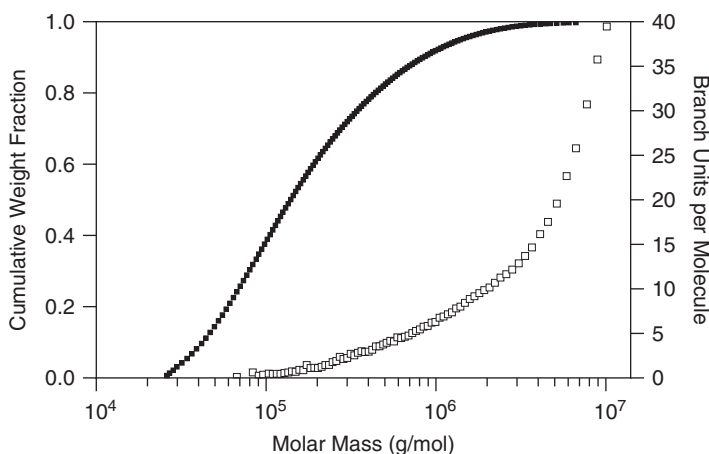


Figure 6.12 Cumulative molar mass distribution plot of randomly branched polystyrene (■) and number of branch units per molecule (□). Branch units calculated from g determined by A4F-MALS (see Figure 6.11).

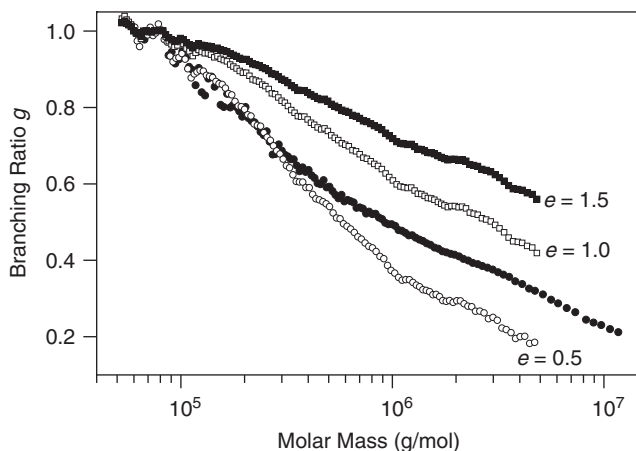


Figure 6.13 Molar mass dependence of branching ratio g determined by radius method (●) and calculated from g' using different values of draining parameter e .

conformation plot (Figure 6.9), and calculated from the Mark-Houwink plot (Figure 6.6) using Equations 6.10 and 6.11 with various values of draining parameter. None of the boundary values of e provide good agreement of results generated from the RMS radii and intrinsic viscosities. The best agreement of the two plots is obtained using e of about 0.7. However, since the parameter e depends on the properties of polymer chain and experimental conditions, no general validity of this value can be assumed.

The comparison of results obtained by the radius and mass methods is depicted in Figure 6.14. Similarly as in the viscosity method, the

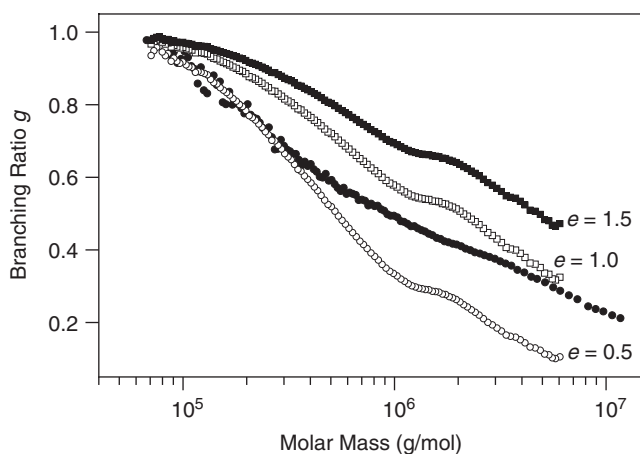


Figure 6.14 Molar mass dependence of branching ratio g determined by radius method (●) and mass method using different draining parameters e .

obtained results strongly depend on the draining parameter and the best agreement of the mass method with the radius method is achieved for e around 0.7.

Although g calculated by means of viscosity and mass methods depends on the value of parameter e and generally does not concur with g obtained by the radius method, with the same e the viscosity and mass methods yield consistent results, as demonstrated in Figure 6.15.

Despite uncertainty of the calculation of g from the intrinsic viscosity due to the commonly unknown parameter e , the intrinsic viscosity has the great advantage of the possibility of measurement of relatively small branched molecules for which the RMS radius cannot be determined. Characterization of lower-molar-mass polymers is demonstrated in Figure 6.16 for star poly(DL-lactic acid) with tripentaerythritol as a branching agent. The RMS radius of such polycondensates is below the detection limit of elastic light scattering and thus the intrinsic viscosity appears as a suitable alternative. The Mark-Houwink plot allows clear detection of branching in the analyzed sample. As molar mass increases, the difference of the intrinsic viscosity between the branched molecules and the linear reference increases, which indicates that molecules of higher molar mass consist of more arms.

Although more detailed analysis of the obtained experimental data regarding the number of arms is limited by the uncertainty of draining parameter e , the data undoubtedly prove the presence of branched macromolecules, and allow mutual comparison of different samples, as well as give a certain feeling of the number of arms. Figure 6.16 also presents the molar mass–versus–elution volume plot that can serve as a simple alternative for branched oligomers when a viscometer is not available.

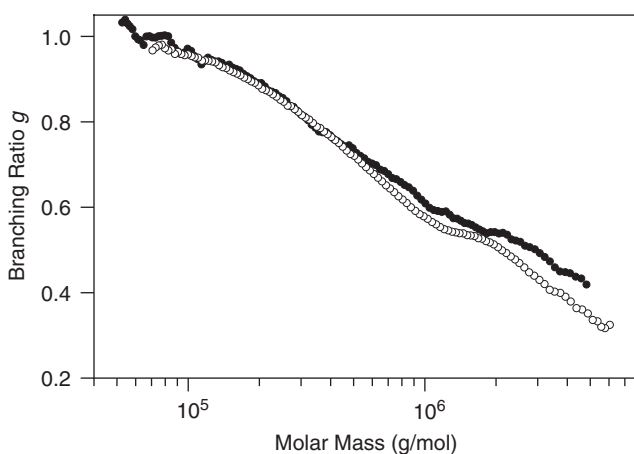


Figure 6.15 Molar mass dependence of branching ratio g determined by viscosity method (●) and mass method (○) using $e = 1$.

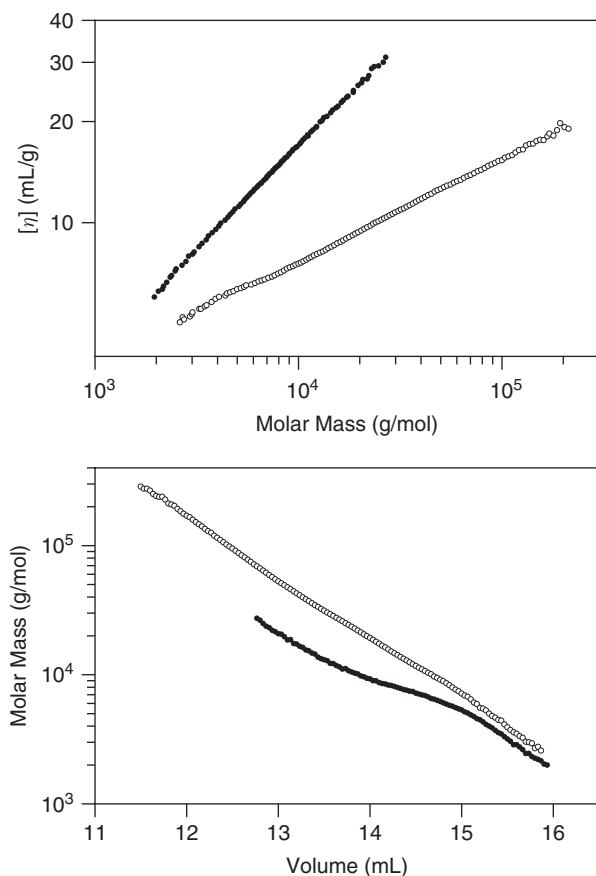


Figure 6.16 Branching analysis of lower-molar-mass polymer: Mark-Houwink plots (top) and molar mass-versus-elution volume plots (bottom) of linear (●) and branched (○) poly(DL-lactic acid).

6.2.3 Average Branching Ratios

A possible advantage of the average branching ratios is that some of the needed information can be obtained by the batch measurements of an unfractionated sample, namely M_w and R_z by classical light scattering and $[\eta]_w$ by a capillary viscometer. Moreover, these averages are not at all or only negligibly affected by the anchoring effect during the SEC separation. The average branching ratios are (1) average branching ratio g_{M_z} calculated for the same M_z , and (2) average branching ratio g'_{M_w} calculated at the same M_w .

The calculation of the average g_{M_z} at the same M_z requires knowledge of R_z and M_z . The former quantity can be obtained by a classical light scattering experiment in the batch mode or by SEC-MALS; the latter can be determined by SEC-MALS. It has been explained that the classical light scattering experiment provides R_z by its fundamental principle and consequently the value of R_z is not influenced by the anchoring effect in SEC column packing. The anchoring effect

on M_z is relatively small, because this quantity counts mainly the high-molar-mass fractions that are not contaminated by molecules delayed by anchoring. In addition to the experimentally determined R_z and M_z the relation between RMS radius and molar mass for the linear polymer of the identical chemical composition must be known. Let us illustrate the calculation on the branched polystyrene (see conformation and Mark-Houwink plots in Figures 6.9 and 6.6, respectively). The experimental results obtained by SEC-MALS are as follows:

$$R_z = 37.0 \text{ nm}$$

$$M_z = 1.24 \times 10^6 \text{ g/mol}$$

The relation RMS radius versus molar mass $R = 0.014 \times M^{0.585}$ can be found in the literature.¹⁵ Using this relation and experimental M_z one can calculate R_z of a linear polymer of the same M_z as that of branched polymer: $R_z = 0.014 \times (1.24 \times 10^6)^{0.585} = 51.4 \text{ nm}$, which yields average branching ratio $g_{M_z} = 0.52$.

A similar calculation leads to the average branching ratio g'_{M_w} at the same M_w :

$$[\eta]_w = 68.4 \text{ mL/g}$$

$$M_w = 370,000 \text{ g/mol}$$

Using the literature¹⁶ Mark-Houwink equation $[\eta] = 0.0117 \times M^{0.717}$, the intrinsic viscosity of a linear polymer having the same M_w as the branched polymer is 115.0 mL/g and consequently average branching ratio g'_{M_w} for the entire sample is 0.59. Note that the average g'_{M_w} can be determined solely by batch measurements with no influence of chromatography separation.

A possible drawback of g_{M_z} is that a part of fractions with very high molar mass can be retained in SEC columns and/or undergo shearing degradation. The R_z and M_z determined by A4F for our branched polystyrene can be used for the sake of demonstration:

$$R_z = 43.7 \text{ nm}$$

$$M_z = 2.27 \times 10^6 \text{ g/mol}$$

Significantly larger R_z and M_z determined by A4F and smaller average g_{M_z} of 0.36 indicate that some of the high-molar-mass fractions were degraded by shear or retained in SEC columns.

Comparison of g_{M_z} and g'_{M_w} for several branched polymers is shown in Table 6.1. It is worth mentioning that the two average ratios are not supposed to be identical, because they are based on different molar mass averages with different sensitivities to the fractions with very high molar mass, and they are mutually related with the draining parameter e , which is generally not equal to unity. It must be also pointed out that g_{M_z} and g'_{M_w} are not true moments of their distribution, and especially g_{M_z} reflects mainly the branching degree of the most-branched fractions (i.e., those with the highest molar mass).

The calculation of the average branching ratios as well as the determination of the relation between g and M require log-log relations R versus M and $[\eta]$ versus

Table 6.1 Comparison of g_{M_z} and g'_{M_w} for Various Branched Polymers Obtained by SEC-MALS-VIS

Polymer	M_w (10^3 g/mol)	g_{M_z}	g'_{M_w}
Randomly branched PS (8)	180	0.71	0.81
Randomly branched PS (9)	220	0.63	0.77
Randomly branched PS (42)	270	0.53	0.71
Randomly branched PS (B1)	250	0.53	0.80
Randomly branched PS (10)	370	0.52	0.59
Randomly branched PS (19)	55	0.49	0.80
Randomly branched PS (40)	330	0.47	0.64
Randomly branched PS (B2)	540	0.45	0.60
Randomly branched PS (20)	80	0.42	0.67
Star PBZMA (197/1)	2,900	0.09	0.09
Star PBZMA (199/1)	2,100	0.09	0.08
Star PS 8-arm	350	0.32	0.51
Brush PS	7,200	0.07	0.04

M for linear polymer of the same chemical composition as the branched polymer under investigation. The latter can be found in the literature for many polymer solvent systems. The published data are not always consistent and careful selection of the literature values and if possible their experimental verification should be carried out. Published relations R versus M are significantly less frequent.

Table 6.2 lists parameters of conformation plots for several common polymers. The determination of the conformation and Mark-Houwink plots requires measurements of a series of narrow standards or a broad polymer sample with polydispersity $M_w/M_n \approx 2$ and more. Narrow standards can be measured either in batch or online mode, whereas broad polymers require online measurement. The necessary condition is that the data cover a sufficiently broad range of molar mass of at least one order of magnitude. It must be noted that measurement of a single narrow polymer can lead to false results and conclusions about branching.

Table 6.2 Constants of Relation $R = k \times M^b$

Polymer	k	b
Polystyrene	0.014	0.585
Poly(methyl methacrylate)	0.012	0.583
Poly(benzyl methacrylate)	0.0114	0.580
Polybutadiene	0.016	0.597
Polyisobutylene	0.0145	0.581
Polyisoprene	0.012	0.611
Polyethylene	0.0186	0.596

Note: THF and room temperature with exception of PE (TCB at 135°C).

6.2.4 Other Methods for the Identification and Characterization of Branching

A certain limitation of the conformation plot based on the RMS radius is the impossibility of characterizing smaller polymers with a majority of molecules with RMS radii below 10 nm. Since the hydrodynamic radius can be accurately determined down to about 1 nm, the relation between the hydrodynamic radius and molar mass (i.e., R_h conformation plot) may become a suitable alternative.

Figure 6.17 shows the conformation plot for a relatively small polymer. Due to the scattering of RMS radii the slope of the conformation plot is determined with high uncertainty. In contrast, the R_h conformation plot appears significantly more reliable and allows accurate determination of the slope. In fact, the same information about the molecular structure can be obtained from the Mark-Houwink plot. However, the R_h conformation plot is a closer equivalent of the RMS radius conformation plot with the slope approximately equal to that based on the RMS radius.

A possible advantage of the R_h conformation plot over that based on the RMS radius is low sensitivity to abnormal SEC elution, as demonstrated in Figure 6.18. In addition, the R_h conformation plot is less sensitive to the light scattering formalisms used for data processing than the RMS radius conformation plot. A conformation plot based on R_h can be determined by SEC-MALS-VIS or SEC-MALS-DLS.

Comparison of the slopes of the conformation plots based on the RMS radius and hydrodynamic radius is shown in Table 6.3, which also includes the slopes of the Mark-Houwink plots. It may be noted that larger differences of the slopes of Mark-Houwink plots of linear and branched polymers compared

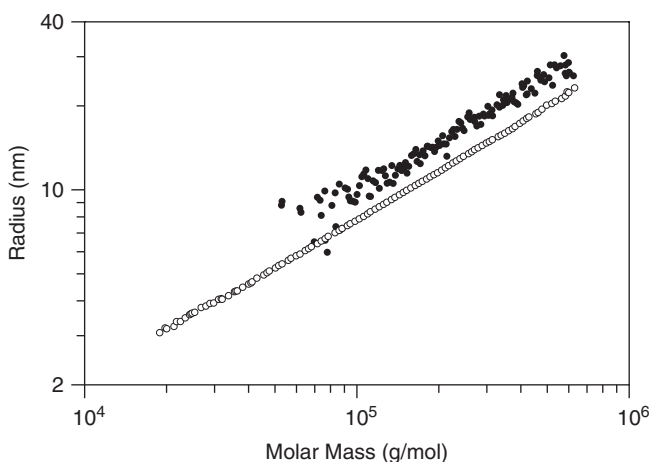


Figure 6.17 RMS radius (●) and hydrodynamic radius (○)–versus–molar mass plots of linear poly(isobutyl methacrylate) determined by SEC-MALS-VIS.

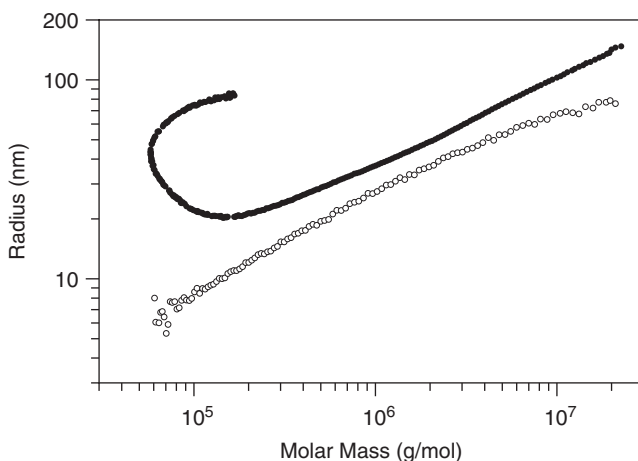


Figure 6.18 RMS radius (●) and R_h (○) conformation plots of randomly branched polystyrene determined by SEC-MALS-DLS.

Table 6.3 Slopes of Conformation Plots Based on RMS Radius and Hydrodynamic Radius and Exponents of Mark-Houwink Relation for Linear and Branched Polymers

Polymer	Slope of Conformation Plot Based on		Mark-Houwink Exponent
	RMS Radius	Hydrodynamic Radius	
Linear PS	0.57	0.57	0.70
Linear PS (NIST 706)	0.57	0.57	0.70
Linear PMMA (Y)	0.57	0.57	0.71
Linear PBZMA (38)	0.57	0.57	0.70
Linear PIBMA	—	0.57	0.73
Randomly branched PS (10)	0.46	0.50	0.51
Randomly branched PS (40)	0.46	0.50	0.50
Randomly branched PS (42)	0.45	0.51	0.51
Star PBZMA (197/1), high f	0.49	0.39	0.15
Star PIBMA, high f	—	0.36	≈ 0

to the differences of the slopes of conformation plots confirm higher sensitivity of the Mark-Houwink plot to detect and differentiate branching.

Burchard et al.¹⁴ suggested the characterization of branching on unfractionated samples and derived theoretical equations for various branched structures. In contrast to g , where the radii are compared either at the same molar mass (in the case of narrow fractions eluting from a separation device) or at the same z -average molar mass (in the case of unfractionated polymer), they came with the definition of g on the basis of R_z at the same weight-average molar mass. A potential advantage of this approach is given by the fact that the quantities R_z and M_w are directly measured by a batch light scattering experiment, while the

z -average molar mass is not directly accessible by light scattering and requires an online fractionation. In contrast to g defined at the same molar mass or M_z , where g decreases with the branching degree and is always smaller than unity, the g defined at the same M_w can be larger than unity and increase with the increasing number of branch units. The explanation of this behavior is that polydispersity causes a larger increase of R_z than the corresponding increase of M_w . The g value is then a result of two counteracting effects: polydispersity, which causes an increase, and branching, which causes a decrease. A typical feature of randomly branched polymers is very high polydispersity, which overwhelms the decrease due to the branching.

Another quantity for the characterization of branching suggested by Burchard et al. is the dimensionless ratio ρ :¹⁴

$$\rho = \frac{R_z}{R_{h,z}} \quad (6.13)$$

where $R_{h,z}$ is the z -average hydrodynamic radius obtained by dynamic light scattering. A potential advantage of the ratio ρ is that it does not require data for linear chains as reference.

The ratio ρ is readily measurable by combination of static and dynamic light scattering. In addition, with the combination of SEC-MALS-DLS(VIS) or A4F-MALS-DLS the ratio ρ can be measured across the molar mass distribution of polymers and thereby indicate the change of polymer architecture along the molar mass axis. The values of the dimensionless ratio ρ were derived for various polymer architectures in theta and thermodynamically good solvents.^{5,14}

The ability of the dimensionless ratio ρ to detect and characterize branching is based on the fact that the two radii are of different definitions and reflect different properties, namely distribution of mass around the center of gravity and the hydrodynamic dimensions. Comparison of RMS radii and hydrodynamic radii of linear polystyrene is presented in Figure 6.19. It may be noted that the difference of R_h based on diffusion coefficient and intrinsic viscosity is small and that the molar mass dependencies of R and R_h are parallel.

Graphical representation of ratio ρ as a function of molar mass for a linear polymer, a randomly branched polymer, and a star polymer with a large number of arms is shown in Figure 6.20. Almost constant values of ρ across the molar mass distribution for the linear chains indicate identical molecular architecture across the molar mass distribution. Decreasing ρ for randomly branched molecules toward high molar masses indicate change of the molecular structure with molar mass as is typical of randomly branched polymers. However, it is not clear why the parameter ρ for the fractions with lower molar mass is larger than in the case of linear molecules. The lowest ρ for the stars consisting of large numbers of arms can be interpreted as a consequence of highly compact molecular structure.

Branching information can be also revealed from the pattern of particle scattering function. Functions $P(\theta)$ for various branched structures can be found in

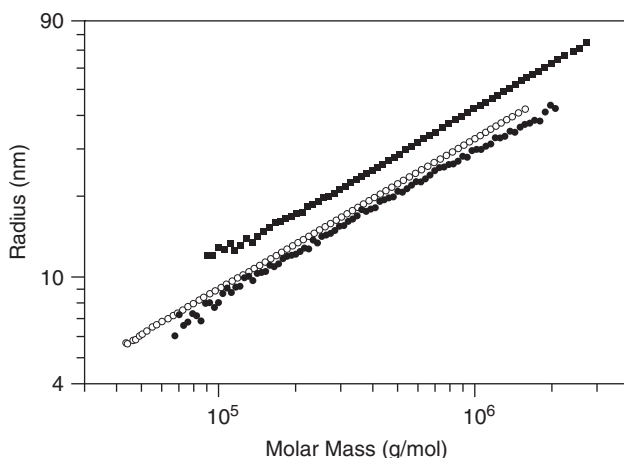


Figure 6.19 Molar mass dependence of RMS radius (■) and hydrodynamic radius determined by DLS (●) and viscometry (○) for linear polystyrene. Data obtained by SEC-MALS-DLS and SEC-MALS-VIS, THF at 25°C.

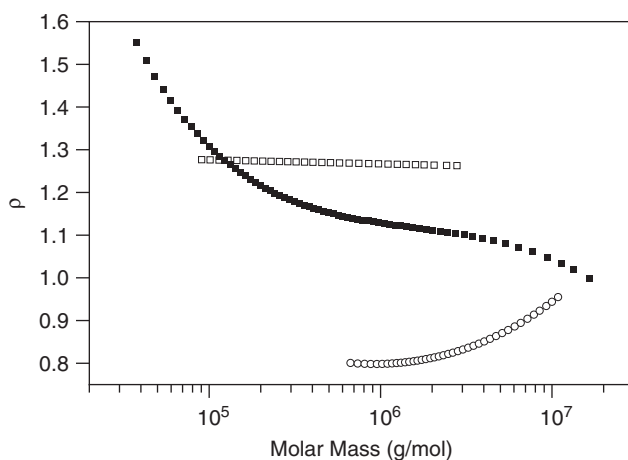


Figure 6.20 Ratio $\rho = R/R_h$ as a function of molar mass for linear polystyrene (□), randomly branched polystyrene (■), and star poly(benzyl methacrylate) of large f (○).

the literature.^{14,17} In order to infer branching information the molecules must have large dimensions, which represents a significant limitation of applicability.

Another possible parameter characterizing the branching degree is the ratio of the weight-average molar mass determined by conventional SEC, $M_w(\text{SEC})$, to the true M_w determined by light scattering. Both $M_w(\text{SEC})$ and M_w can be obtained in a single SEC-MALS experiment when the obtained RI signal is processed also using the column calibration. The ratio $M_w(\text{SEC})/M_w$ is certainly the least fundamental parameter describing the degree of branching that has no direct

relation to the number of branch units or arms in branched macromolecules. However, it may appear useful especially in the case of smaller branched polymers that are characterized by SEC-MALS without a viscometer. Since SEC separates molecules according to their hydrodynamic volume, the elution volume itself bears information about the molecular size, and consequently the $M_w(\text{SEC})$ calculated from a calibration curve is related to the average hydrodynamic size. If polystyrene calibration is used for data processing, the $M_w(\text{SEC})$ can be interpreted as the weight-average molar mass of a hypothetical sample of polystyrene having the same distribution of hydrodynamic volume as a polymer under investigation. Similarly to g and g' , the ratio $M_w(\text{SEC})/M_w$ decreases with increasing degree of branching. However, depending on the relation between the calibration applied for data processing and the true calibration for a polymer under investigation, the ratio $M_w(\text{SEC})/M_w$ for a linear polymer may be larger or smaller than unity.

6.3 EXAMPLES OF CHARACTERIZATION OF BRANCHING

It has been shown that there are several possible methods useful for the characterization of polymer branching. Some of them are of rather theoretical applicability and their real ability to provide information about the branching seems to be limited. That is the case with the particle scattering function, which can provide structural information only for very large macromolecules. Additional experimental data may be needed to further verify the usability of parameter ρ , because not all results appear as straightforward as those shown in Figure 6.20. Some methods are purely empirical and have no direct relation to branched structure, such as the ratio $M_w(\text{SEC})/M_w$. However, simplicity and applicability over broad molar mass range is the great advantage of this ratio, which can be readily determined by combination of conventional SEC and SEC-MALS.

The conformation plot appears to be the soundest way to obtain branching information, but it is significantly restricted by the impossibility of studying smaller molecules and moreover by frequently poor SEC separation of large, highly branched macromolecules. Consequently, the combination of A4F with MALS appears to be the most efficient method for branching studies of larger macromolecules, while for smaller branched molecules SEC-MALS-VIS will usually be the best choice. However, there is no general method for branching characterization. The results obtained by the particular methods need not be identical, but they should provide the same trends. The combination of results obtained by different methods may confirm the presence or absence of branching and indicate the structure of branched molecules. For successful branching investigation it is important to understand the limits and realize that really detailed characterization is usually impossible, and that any obtainable information may be valuable. The purpose of this chapter is to show several typical examples of data for various branched polymers, which should facilitate proper interpretation of the reader's own experimental results and help avoid making false conclusions.

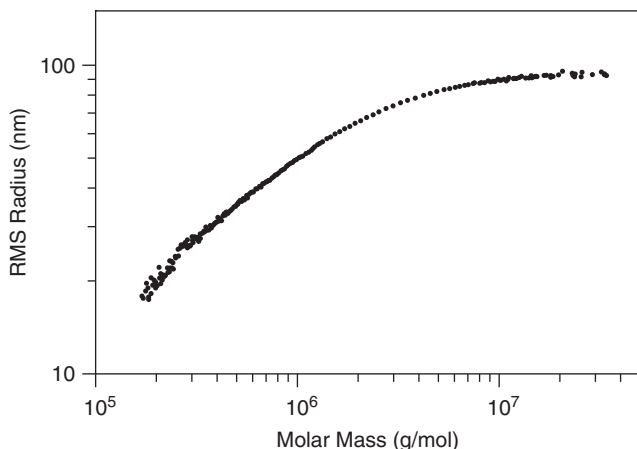


Figure 6.21 Conformation plot of randomly branched polymer with slope leveling off toward high molar masses.

Figure 6.21 is an example of a conformation plot with the slope decreasing toward high molar masses. At the high-molar-mass end, the conformation plot reaches a plateau, which means that a further increase of molar mass is absorbed inside the polymer coil without increase of molecular size. This pattern of conformation plot is typical for randomly branched polymers containing high-molar-mass fractions with high degree of branching.

Figure 6.22 shows an example of Mark-Houwink plot for a linear oligomer. The slope of about 0.5 could lead to a false conclusion of the presence of branching. However, the slope of the Mark-Houwink plots of linear oligomers is close to 0.5 even in thermodynamically good solvents, since the excluded volume

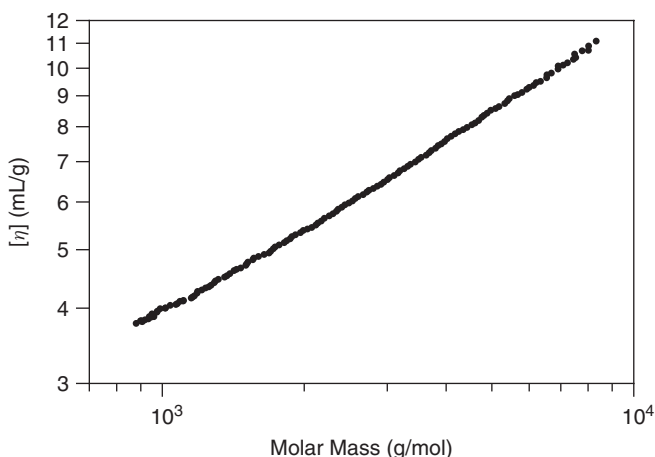


Figure 6.22 Mark-Houwink plot of linear oligoester: Mark-Houwink exponent $a = 0.48$.

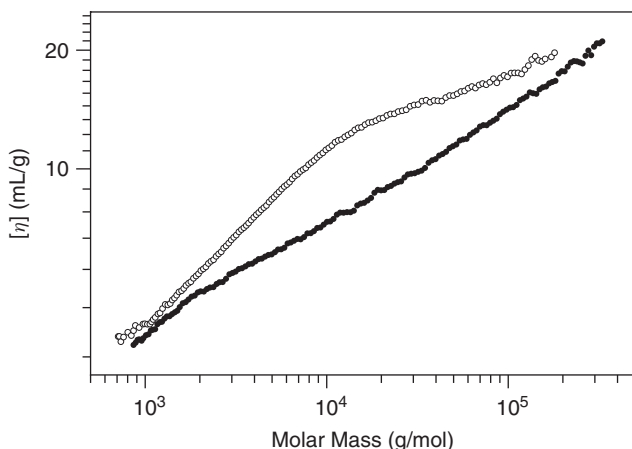


Figure 6.23 Mark-Houwink plots of unsaturated polyester resins of different distributions of branching.

effect is absent in the case of oligomeric chains that are too short to obey the intramolecular self-avoiding behavior.

Figure 6.23 depicts Mark-Houwink plots for two unsaturated polyester (UP) resins. One of the UP resins prepared from difunctional monomers (○) shows different slopes of the Mark-Houwink plot. The slope up to the molar mass of about 10,000 g/mol is roughly 0.5, which is in good agreement with the Mark-Houwink exponents for model UP resins that were prepared with maleic anhydride replaced with succinic acid that has no double bond capable of side reactions. Above a molar mass of about 10,000 g/mol the slope is significantly lower (≈ 0.16),

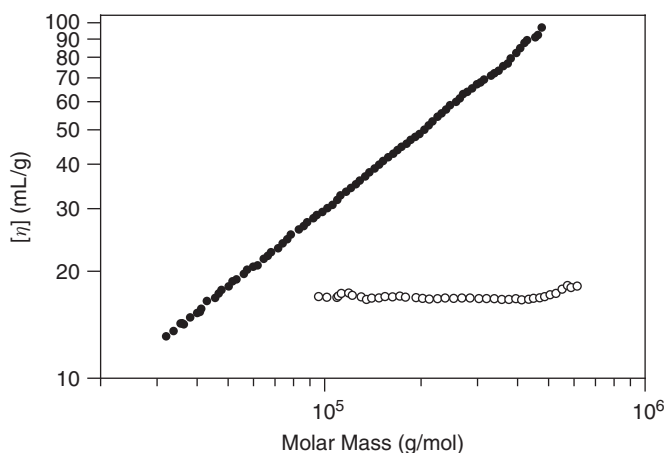


Figure 6.24 Mark-Houwink plots of linear (●) and star high- f (○) poly(isobutyl methacrylate). Zero slope indicates compact sphere-like structure of star macromolecules.

which can be explained by side reactions of double bonds of maleic anhydride leading to formation of branched molecules. The second UP resin (●), which was prepared with an addition of six-functional dipentaerythritol, shows a markedly lower Mark-Houwink exponent of ≈ 0.26 from the region of low molar masses. In this resin the addition of polyfunctional monomer resulted in the formation of branched molecules from the beginning of molar mass distribution.

Figure 6.24 compares the Mark-Houwink plot of linear poly(isobutyl methacrylate), PIBMA, with that of star-branched PIBMA with high numbers of arms prepared by GTP. The plot of linear PIBMA is linear as is characteristic of linear polymer with typical slope of ≈ 0.7 , while the slope of the star PIBMA is close to zero, which indicates a highly compact molecular structure resembling compact spheres.

Another example of Mark-Houwink plots with the slopes in proximity to zero is shown in Figure 6.25 for a series of high- f star-branched polymers. The mutual shift of the plots along the axis of intrinsic viscosity indicates different compactness of the sphere-like macromolecules. It is worth noting that the Mark-Houwink

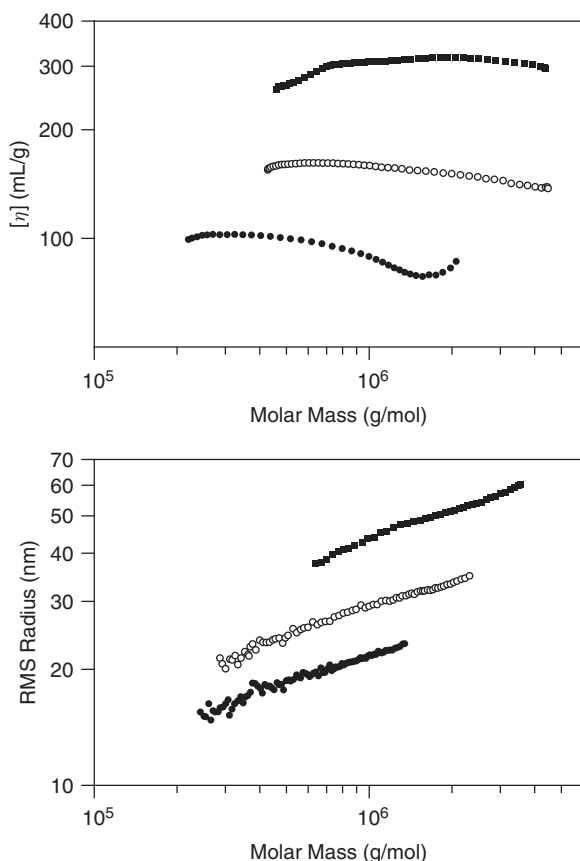


Figure 6.25 Mark-Houwink plots with the slopes close to zero for highly branched sphere-like polymers (top) and the corresponding conformation plots obtained by A4F-MALS (bottom). Slopes of the conformation plots ≈ 0.23 .

plots show regions of decrease of the intrinsic viscosity with increasing molar mass. Such behavior was described for dendrimers¹⁸ and explained as due to the polymer growing faster in density than in radial growth, when the intrinsic viscosity initially increases with molar mass, reaches a maximum, and then steadily decreases with increasing molar mass. The Mark-Houwink plots are completed by the corresponding conformation plots with the slopes confirming compact sphere-like structure of the analyzed molecules.

Figure 6.26 shows conformation and branching ratio g –versus–molar mass plots for starlike poly(benzyl methacrylate) prepared by GTP. Unlike the g –versus– M plot of randomly branched polymers (e.g., Figure 6.11), the plot in this figure starts at very low g and further decreases with increasing molar mass. This indicates that the sample does not contain, with the exception of residual unreacted arms that are not included in the plot, linear molecules. That is a significant difference compared to randomly branched polymers that typically contain a large part of linear molecules of lower molar mass. According to

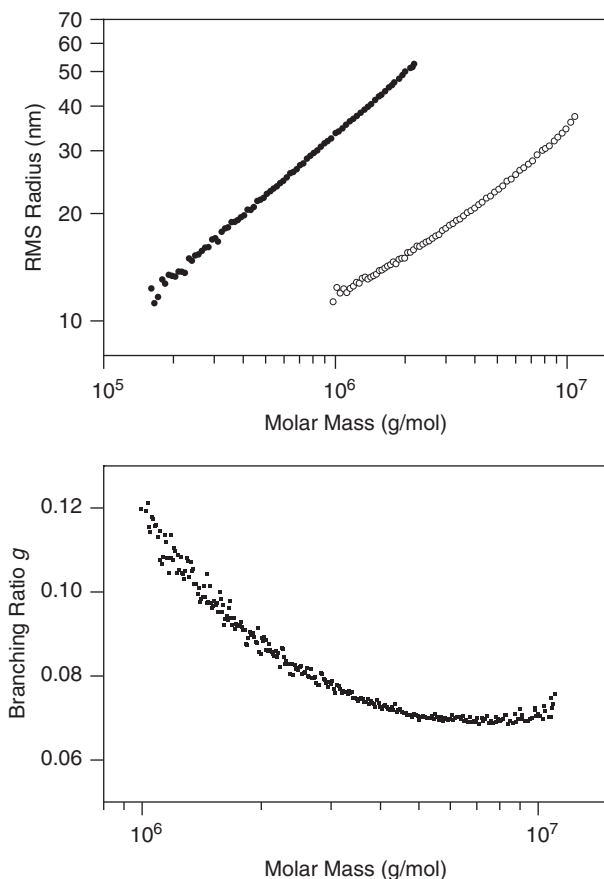


Figure 6.26 Conformation plots of linear (●) and star high- f (○) poly(benzyl methacrylate) (top) and branching ratio–versus–molar mass plot (bottom).

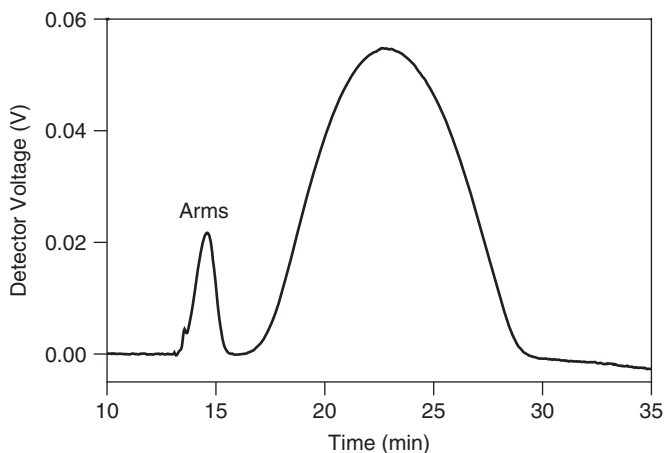


Figure 6.27 A4F RI fractogram showing separation of unreacted arms from stars for poly(benzyl methacrylate) prepared by GTP. Conformation and g -versus- M plots are shown in Figure 6.26.

Equation 6.8, the branching ratio g of 0.1–0.07 corresponds to about 60–80 arms. The presence of unreacted arms (see Figure 6.27) in the sample and the determination of their molar mass allow the estimation of number of arms by dividing M_n of stars and arms. This results in an average number of about 70 arms, which is in very good agreement with the value estimated from g .

Figure 6.28 compares conformation plots of two branched polystyrene samples. The plot of one of the samples is shifted to lower RMS radii, which can be explained by higher branching degree and thus higher polymer coil density. The

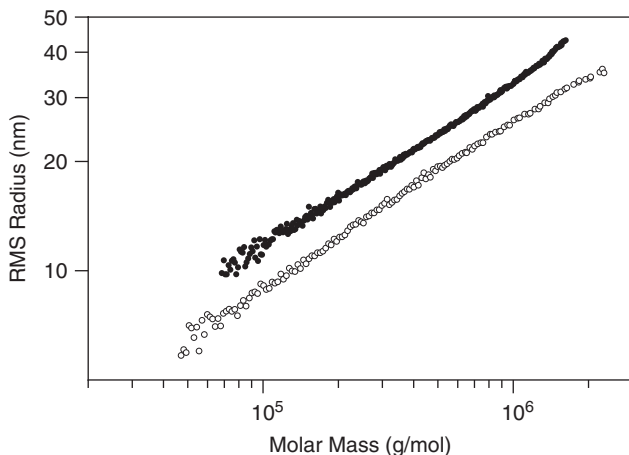


Figure 6.28 Conformation plots of two randomly branched polystyrene samples prepared using identical amounts of divinylbenzene (0.5% wt), but different initiator concentrations, namely 0.1% (●) and 1% (○). Conversion: 26% and 63% for initiator concentration of 0.1% and 1%, respectively.

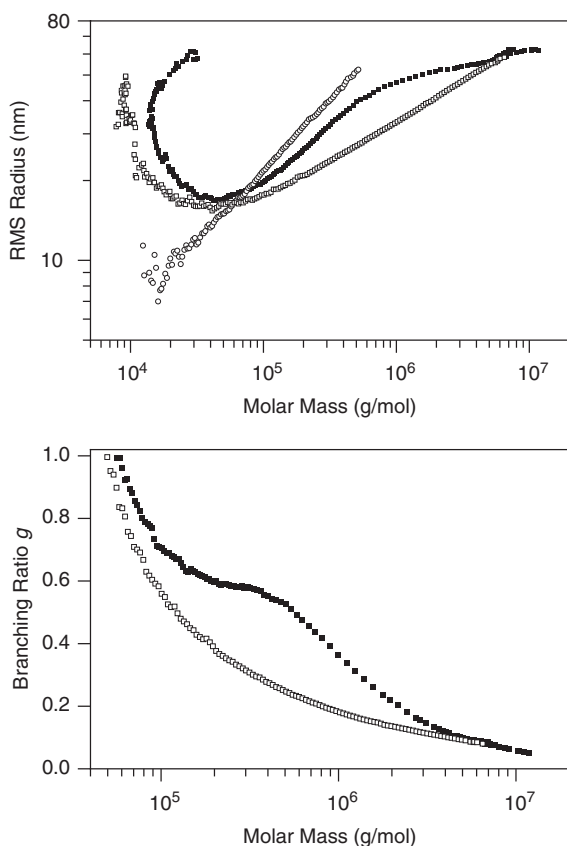


Figure 6.29 Conformation plots (top) and g -versus- M plots (bottom) of linear polyethylene NIST SRM 1475 (o) and two branched polyethylenes: NIST SRM 1476 (■) and a commercial sample (□). Columns $3 \times$ PLgel Mixed-B, TCB at 1 mL/min, 160°C .

samples were prepared using identical levels of branching co-monomer (divinylbenzene), but different concentrations of initiator of radical polymerization. The higher radical concentration resulted in higher conversion of divinylbenzene (i.e., higher number of branch units), and also shorter chains due to termination by recombination of growing radicals.

Figure 6.29 contrasts conformation plots of three polyethylenes and the branching ratios of the two branched samples. The conformation plots of both branched samples cross that of linear polyethylene and show typical upturn in the region of lower molar masses. Except for the upturn, the conformation plot of standard NIST SRM 1476 polyethylene (■) can be separated into two regions with different slopes suggesting different branching topology, while the slope of the commercial sample (□) is approximately constant. The obtained data indicate that up to molar mass of about 5×10^6 g/mol, NIST SRM 1476 is less branched than the commercial sample since its conformation plot is shifted to higher RMS radii and the branching ratio is larger. At the region of high molar masses the

plots of the two branched polyethylenes meet each other, which indicates similar degree of branching.

6.4 KEYNOTES

- The fundamental principle of branching characterization is based on the fact that branching reduces molecular size.
- The molar mass and a parameter characterizing molecular size are necessary to determine the degree of branching.
- The effect of long-chain branching on the size of branched macromolecules in dilute solution is characterized with parameter g , which is defined as the ratio of the mean square radius of a branched molecule to that of a linear molecule at the same molar mass. The parameter g decreases with increasing degree of branching and can be used to calculate the number of branch units or number of arms in branched molecules. An alternative branching ratio g' is defined as the ratio of the intrinsic viscosity of a branched molecule divided by the intrinsic viscosity of a linear molecule at the same molar mass. The branching ratios g and g' are related via the draining parameter e , whose values are supposed to be in the range 0.5–1.5. However, the exact e values are usually unknown.
- SEC-MALS, A4F-MALS, and SEC-MALS-VIS data can be processed in three different ways to detect the presence of branched molecules and get information about the distribution of branching with respect to molar mass. The branching ratio g can be obtained from (1) conformation plot, (2) molar mass–versus–elution volume plot, and (3) Mark-Houwink plot.
- Two average branching characteristics g_{M_z} and g'_{M_w} can be calculated, the latter being obtainable even without chromatographic separation. In addition, the ratio $M_w(\text{SEC})/M_w$ can be used as a simple parameter capable of identifying branching and differentiating branching degree of polymers of identical chemical composition.
- The conformation plot, which is the most direct way to obtain parameter g and further branching characteristics, is often affected by the anchoring of branched molecules in the pores of SEC column packing. Anchoring increases the polydispersity of slices at the region of higher elution volumes. Since polydispersity causes a larger increase of the z -average RMS radius compared to the weight-average molar mass, the conformation plots become upward at the region of lower molar masses.
- A crucial requirement for the determination of a true conformation plot is that the molecules eluting from the separation device are almost monodisperse. For many large branched polymers this requirement is not fulfilled using SEC due to the anchoring effect in the pores of column packing. The anchoring effect is totally eliminated in the case of A4F, where the separation occurs in an empty channel and such highly efficient separation

of branched molecules is achieved resulting in perfectly linear conformation plots with no artifacts. Another requirement for the determination of accurate conformation plot is avoiding the marginal scattered data points.

- Lower sensitivity to the anchoring effect and the possibility of characterizing small branched polymers are advantages of the SEC-MALS-VIS measurements.

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