Quantification of Branching in Disordered Materials

A. S. KULKARNI, G. BEAUCAGE
Department of Chemical and Materials Engineering, University of Cincinnati,
Cincinnati, Ohio 45221-0012

Received 11 February 2005; revised 30 September 2005; accepted 16 February 2006
DOI: 10.1002/polb.20794

ABSTRACT: The phenomenon of structural branching is ubiquitous in a wide array of materials: polymers, ceramic aggregates, polymeric networks, and gels. Branching has a strong influence on the structure–property relationships of these materials. Despite the interdisciplinary importance and decades of effort, the analytical description and quantification of branching are weak. Existing techniques for polymers based on size exclusion chromatography and rheology are, at best, qualitative, and quantitative characterization techniques such as nuclear magnetic resonance spectroscopy and transmission electron microscopy (for ceramic aggregates) have limitations in providing routine quantification. For ceramic aggregates, theoretical work has dominated, and only a few publications on analytical studies exist to support the theory. Small-angle scattering of X-rays and neutrons can be used to quantify the branch content through application of concepts native to fractal geometry. © 2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 1395–1405, 2006

Keywords: branched; ceramic aggregates; polyethylene (PE); small angle neutron scattering; small-angle X-ray scattering

AMIT KULKARNI
GREG BEAUCAGE

Amit Kulkarni is a Ph.D. candidate in the Department of Chemical and Materials Engineering at the University of Cincinnati. His work is focused on the study of branched polymers and ceramic aggregates as well as phase separation in network systems driven by branching. Kulkarni holds a B.S. degree in Polymer Engineering from the University of Pune (India) and an M.S. degree in Materials Science and Engineering from the University of Cincinnati.

Greg Beaucage is an Associate Professor of Chemical and Materials Engineering at the University of Cincinnati. He is a recognized expert in small-angle scattering, having chaired the small-angle scattering group at the American Crystallographic

---

Correspondence to: G. Beaucage (E-mail: beaucag@uc.edu)

Journal of Polymer Science: Part B: Polymer Physics, Vol. 44, 1395–1405 (2006)

Association and having been an officer in that organization. He is on the advisory board for the Intense Pulsed Neutron Source at Argonne National Laboratory and has more than 100 peer-reviewed publications. His B.S. degrees in Zoology and Chemical Engineering are from the University of Rhode Island, and he obtained his Ph.D. degree in Polymer Science and Engineering from the University of Massachusetts at Amherst under Dick Stein. Beaucage worked for a short time at Sandia National Laboratories in Albuquerque but has spent the majority of his career at the University of Cincinnati, except for a 1-year sabbatical in Zurich at Eidgenössische Technische Hochschule (ETH) in process engineering, where he studied the pyrolytic growth of nanoparticles, using X-ray and light scattering. His interests span a wide range of fields, but much of his work has been focused on disordered materials, including the quantification of branched structures in polymers, networks, and aggregates, especially with small-angle X-ray and neutron scattering.

INTRODUCTION

Ramified structures are common in a variety of materials, including polymers and ceramic aggregates. Polymers, for example, are generally described by their chemical structure and their molecular weight distribution (MWD). Branching can be considered the next most important characteristic feature influencing the properties of polymers. The presence of a few short-chain branches drastically changes the crystallization behavior of semicrystalline polymers.[1] The presence of long-chain branching (LCB) has a direct bearing on the hydrodynamic and rheological properties of polymer solutions and melts. Phase separation has been reported in commercial polymers because of a disparity in the branch contents of constitutive fractions.[2–11] On similar lines, phase separation in a network structure[12] has been observed as a result of branching/crosslinking differences of one of the components in multicomponent systems.

Branching/aggregation plays a major role in deciding the reinforcing properties of particulate fillers such as silica and carbon black in filled elastomeric systems.[13–17] The obtained reinforcement is theoretically linked to the structure of the aggregated filler particles,[18] along with their interaction with the elastomer matrix. In general, highly branched/aggregated filler particles provide optimum reinforcing characteristics.[13] Details concerning reinforcement depend on the fractal dimension (d_f) and branch fraction (ϕ_{br}).[13,18,19]

Branching in polymers and aggregates can be classified as regular or random branching (Fig. 1).[15] Regularly branched polymers include architectures described as comb polymers, star polymers, and dendritic polymers. These branches are obtained in a controlled manner, and these polymers often display colloidal (e.g., micellar) properties. The discussion of such regularly branched structures and their quantification is beyond the scope of this article. The focus of this review is randomly branched polymers in which the insertion of branches is statistical. Readers are referred to the work of Lohse et al.[20] for a detailed study of the effects of branching as manifested in the rheological properties of such polymers, as shown in their exhaustive study of model/regularly branched systems.

Branches in polymers/aggregates can also be classified as short or long. The question of how long a long branch should be before it is classified as a long branch is a topic of some controversy.[21–25] We think that a long branch is one that is indistinguishable from the main chain. This provides an unambiguous way of distinguishing between short- and long-chain branches. For the most part, this review considers LCB, although there may be some possibility of extension to short-chain branching (SCB) in approximation. Only a few key examples are discussed, with the goal of encompassing the exhaustively studied field of quantifying statistical long-chain-branched structures with routes well established in the current literature.

Comparisons between existing techniques to quantify branching/aggregation are outlined in Table 1. Relative measures of branching obtained from size exclusion chromatography (SEC) and rheological measurements are routinely used for estimating branching in polymers. Nuclear magnetic resonance (NMR) spectroscopy has also been employed for determining the branch content in polymers through the detection of the frequency shifts for carbon atoms at branch points

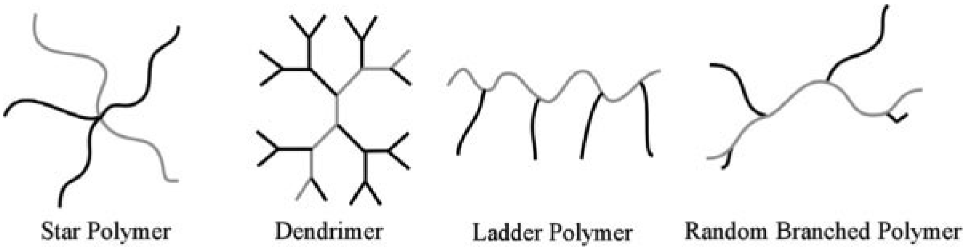


Figure 1. Different branched structures. The gray indicates p.

by high-frequency ^{13}C NMR and by ^{29}Si NMR in silica-based ceramics.[26] Transmission electron microscopy (TEM) can be used to obtain the degree of aggregation in diffusion/reaction-limited aggregates. An analysis of the viability of these techniques for estimating branching/aggregation from existing literature and their shortcomings is presented.

DETERMINATION OF THE BRANCH CONTENT IN POLYMERS BY SEC

SEC [gel permeation chromatography (GPC)] has widely found applications as an indirect/relative technique for characterizing MWD in polymers. It reveals the molecular weight of a polymer fraction by the detection of its hydrodynamic volume[27–30] [which is given as the product of the intrinsic viscosity ($[\eta]$) and viscosity-average molecular weight] by comparison with a calibration curve of standard polymers of known MWD. By the measurement of $[\eta]$ with an inline viscometer and refractive-index detector, the viscosity-average molecular weight of the polymer fraction can be readily calculated.[28,29]

SEC separates a polydisperse polymer sample on the basis of the hydrodynamic sizes of different fractions and not their molecular weights.[28,29] That is, it cannot differentiate between a branched polymer and a linear polymer of equal size, which would elute out at the same time. For a linear polymer and a branched polymer of equal molecular weight, the radius of gyration (R_g) of the branched molecule will be smaller,[28] as the schematic in Figure 2 shows.

Historical Preview

According to Zimm and Stockmayer,[31] the ratio of the mean square radii of gyration of a branched polymer and a linear polymer of equal molecular weight is known as the parameter g and is related to the parameter g', which is the ratio of the $[\eta]$ values of a branched polymer and a linear polymer:[28–31]

$$g' = g^e \tag{1}$$

where g is equal to $\langle R_g^2\rangle_b/\langle R_g^2\rangle_l$, g' is equal to $[\eta]_b/[\eta]_l$, e is a scaling constant, $\langle R_g^2\rangle$ is the mean square radius of gyration, and the subscripts b and l refer to the branched and linear polymers. (For a Gaussian chain, $R_g^2 \sim m$, where m is the degree of polymerization, and for low polydispersity, $V \sim R_g^3$. Therefore, $[\eta] \sim 1/\rho \sim V/m \sim R_g$, and $g' \sim (R_g)_b/(R_g)_l \sim g^{1/2}$; $e = 1/2$ (V is the volume and ρ is the density). Zimm and Stockmayer[31] generalized this for non-Gaussian chains with a higher polydispersity *ad hoc* in eq 1 and ignored the scaling prefactors.) The $[\eta]$ and molecular weight values measured in an SEC experiment correspond to the

Table 1. Comparison of the Different Characterization Techniques Used in the Quantification of Branching[a]

	Technique	Effective in Measuring LCB	SCB	Nature	What They Measure[a]	System
1	SEC	Yes	No	Relative	Qualitative	Polymers
2	NMR	No	Yes	Absolute	$\langle n_{br}\rangle$, $\langle L_{br}\rangle$	Polymers + ceramics
3	Rheology	Yes	No	Relative	Qualitative	Polymers
4	TEM	Not applicable		Absolute	n_{br}, L_{br}	Ceramics
5	Scattering	Yes	Possible	Absolute	ϕ_{br}, c, d_f	Polymers + ceramics
6	Gas adsorption	Averaging technique		Absolute	$\langle S/V\rangle_{primary}$	Ceramics

[a] L_{br} = length of branches; $\langle S/V\rangle_{primary}$ = surface-to-volume ratio of primary particles.

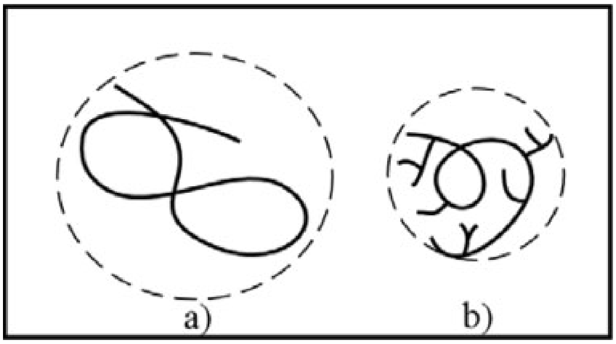


Figure 2. Comparison of the radii of gyration of (a) a linear polymer and (b) a branched polymer of equal molecular weight.

actual branched molecule being run through the column. The corresponding value of $[\eta]$ for a linear polymer of the same molecular weight can be calculated with the Mark–Houwink equation:

$$[\eta]_l = KM^a \tag{2}$$

where M is the molecular weight and K and a are constants for a given polymer–solvent pair. Once the parameter g is obtained, the Zimm–Stockmayer relationship (eq 3)[31] is used to estimate the branch content. To use the correct relationship, knowledge of the nature of branching, that is, whether the branch points are trifunctional or tetrafunctional and whether the branch lengths are random or monodisperse, is needed.[28–30] For polydisperse branch lengths with trifunctional branch points, g is given as follows:[28–31]

$$\langle g_3 \rangle_{\rm w} = \frac{6}{n_{\rm w}}\left\{1/2\frac{(2+n_{\rm w})^{1/2}}{(n_{\rm w})^{1/2}}\ln\frac{(2+n_{\rm w})^{1/2}+(n_{\rm w})^{1/2}}{(2+n_{\rm w})^{1/2}-(n_{\rm w})^{1/2}}-1\right\} \tag{3}$$

where the subscripts 3 and w indicate trifunctional branch points with polydisperse branch lengths and $n_{\rm w}$ is the weight-average number of branches per molecule. The branching can then be quantified with the following relationship, which in this case is for polyethylene:[29]

$$\frac{\rm LCB}{1000\,C} = \frac{n_{\rm w}}{M}(14{,}000) \tag{4}$$

where 14,000 corresponds to the molecular weight of 1000 repeat units of a —(CH$_2$)— molecule.

Recent Works

Although SEC provides an empirical technique for estimating the long-chain-branch content as well as distribution, it remains a relative technique involving indirect calculations based on iterative solutions for eqs 1 and 3.[30] SEC experiments are carried out in good solvents, whereas the Zimm–Stockmayer relationships were derived for theta solution conditions ($e = 1/2$). The effect of these assumptions on different branched polymer systems is not known. The accuracy, as of any SEC method, is dependent on the sensitivity of its detectors (Fig. 3). Molecular-weight-sensitive detectors such as viscometer detectors and light scattering detectors show a poor response in the low-molecular-weight tail of the chromat-

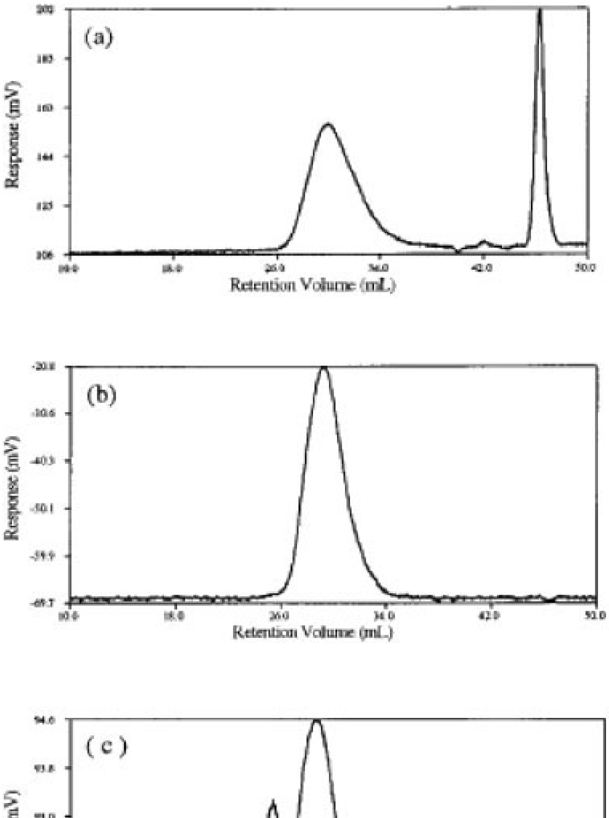


Figure 3. Response versus the retention volume for (a) a refractive-index detector, (b) a viscometer detector, and (c) a light scattering detector for the same sample.[32] Reprinted with permission from Beer, F.; Capaccio, G.; Rose, L. J. J Appl Polym Sci 1999, 73, 2807.

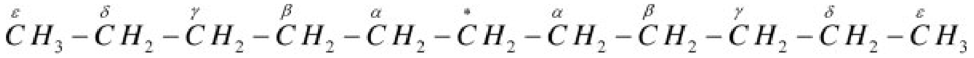
ogram, whereas concentration-sensitive detectors such as differential refractive-index detectors show a poor response in the high-molecular-weight slice of the raw data.[32] The advent of multidetector configurations seems to have overcome some of these difficulties with the direct determination of both R_g and $[\eta]$ as a function of the molecular weight without the necessity of resorting to a calibration curve. Some efforts have also been made toward using a distribution of the parameter $\langle g_3 \rangle_w$ instead of the single weight-averaged value given by eq 3,[33] although the results do not provide an unambiguous determination of the branch content. The reduction in $[\eta]$ of a branched polymer, as opposed to a linear polymer, is the basis of the branch content measurement in SEC. This reduction in $[\eta]$ due to short branches is only 0.01 times that due to long-chain branches.[28] Hence, the sensitivity of the SEC branch content is limited to high levels of LCB, for which comparative data is lacking, as discussed later.

DETERMINATION OF THE BRANCH CONTENT IN POLYMERS AND CERAMICS BY NMR

Among commercial polymers, the determination of the branch content by NMR spectroscopy has been exhaustively studied for two polymers: polyethylene and poly(vinyl chloride) (PVC).[34–38] High-resolution ^{13}C NMR has ben used for this application. With this technique, shifts in the radio-frequency vibrations of up to five carbon atoms from a branch point have been estimated[39] and can be used to calculate the number density of branches. For polymers other than polyethylene, extensive sample preparation may be necessary. The estimation of branching in PVC, for example, requires the removal of the Cl atoms by a process of reductive dechlorination with lithium aluminum hydride[40] or tributyl tin hydride[41] to negate the complex effect of stereochemical isomerization.[32] After this procedure, determining branching in PVC with ^{13}C NMR spectroscopy is similar to determining branching in polyethylenes, as described later. One drawback of NMR is that it cannot differentiate between branches composed of six carbon atoms or more and hence assigns them all as long branches. The main drawback is that the technique counts for the most part the number of branch sites, and these are very few in long-chain-branched systems in which the rheological consequences of branching are large.

Grant and Paul Chemical Shifts

The Grant and Paul empirical relationship[42] can be used to assign chemical-shift values for carbon atoms in a branched hydrocarbon polymer. It was developed with chemical-shift values from alkanes. The chemical shift of any carbon atom in ^{13}C NMR can be decomposed as a sum of contributions from its nearest five neighboring carbon atoms. For *n*-undecane



$$\overset{\varepsilon}{C}H_3-\overset{\delta}{C}H_2-\overset{\gamma}{C}H_2-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-\overset{*}{C}H_2-\overset{\alpha}{C}H_2-\overset{\beta}{C}H_2-\overset{\gamma}{C}H_2-\overset{\delta}{C}H_2-\overset{\varepsilon}{C}H_3$$

the chemical-shift value for *C is given as follows:

$$\text{Chemical Shift} = 2(\alpha + \beta + \gamma + \delta + \varepsilon) + C \qquad (5)$$

where α, β, γ, δ, and ε are called Grant and Paul parameters and C is a constant. The values are outlined in Table 2.[42]

When applying the Grant and Paul relationship to branched polymers, we must account for a correction due to the molecular geometry of bonded neighbors. These corrections are shown in Table 3.[42] 3°, 2°, and 1° represent tertiary, secondary, and primary carbon atoms (Fig. 4), and 3° (2°) represents the correction for a tertiary carbon bonded to a secondary carbon, as in a methine group to a methylene. However, Randall[43] showed that the Grant and Paul parameters are temperature-dependent and gave corrected values for these parameters by conducting ^{13}C NMR for hydrogenated polybutadiene with 183 branches per 1000 carbon atoms.

Recent developments seem to have increased the detectable branch length up to 10 carbon atoms.[44] Liu et al.[44] demonstrated that it is possible to assign chemical-shift values to atoms in a side chain greater than six carbon atoms with ultrahigh-frequency ^{13}C NMR (188.6 MHz).

Using NMR in quantifying the branch content has a drawback: the results for the branch content will always overestimate LCB, that is, branches larger than about six carbon atoms. Hence, the sensitivity of NMR for determining the branch content is limited to high levels of SCB. However, NMR is an effective tool for the determination of the total number of branch sites (n_{br}) in a polymer chain. In this way, it is somewhat analogous to TEM for ceramic aggregates, except that TEM does not measure average values for n_{br} very well (Table 1).

Table 2. Grant and Paul Parameters Obtained from Alkanes[a]

Grant and Paul Parameter	Shift (ppm)
α	8.61
β	9.78
γ	−2.88
δ	0.37
ε	0.06
C	−1.87

[a] The values were taken from ref. 42.

^{29}Si NMR is used to characterize the intermediate chemical species formed during the hydrolysis condensation reaction en route to the formation of silicate aggregates.[26] These intermediates can take on various topological forms ranging from linear to branched to ring structures. The final topological structure of the aggregate, however, cannot be determined by NMR, which can be determined by scattering techniques.

DETERMINATION OF LCB IN POLYMERS WITH RHEOLOGY

Although NMR is an extremely sensitive quantitative technique for counting branch sites, it has the same drawback as TEM for ceramic aggregates: it is much less sensitive to/or cannot quantify the main feature of branching that affects properties, that is, the volumetric contribution of branches to aggregates or to polymer chains:[19]

$$\phi_{\mathrm{br}} = (z - p)/z \tag{6}$$

where p is the occupied volume or mass of a minimum (conducting) path across the aggregate and z is the occupied volume or mass of the entire structure. Because this feature is critical to the rheology of polymers, it is natural that attempts have been made to use rheology to quantify branching.

The presence of LCB has a profound effect on the rheological properties of polymers,[45–51] especially metallocene-catalyzed polyethylenes.[52–60] Only LCB of the order of 2–3 times the entanglement molecular weight[21–25] strongly affects rheological behavior.

The Dow rheology index (DRI) has been proposed as an indicator of the branching level in industrial polymers.[61] For linear polyethylene, the Cross equation[45,61] gives a relationship between the viscosity (η) and shear rate ($\dot{\gamma}$):

$$\eta\left(\dot{\gamma}\right) = \frac{\eta_0}{1 + \left(\lambda\dot{\gamma}\right)^n} \tag{7}$$

where η_0 is the zero-shear-rate viscosity and λ is the characteristic time ($3.65 \times 10^5\ \lambda = \eta_0$). The DRI is obtained as follows:

$$\mathrm{DRI} \equiv [3.65 \times 10^5(\lambda/\eta_0) - 1]/10 \tag{8}$$

DRI is 0 for linear polymers and has positive values for branched polymers. DRI is applicable only to polymers with a narrow MWD (weight-average molecular weight/number-average molecular weight < 2) because it cannot differentiate the effects of polydispersity and branching.

The long-chain-branching index (LCBI) proposed by Shroff and Mavridis[46] attempts to overcome the shortcomings of the DRI. Shroff and Mavridis[46,62] used the Zimm–Stockmayer relationship[31] to derive an expression for LCBI under the assumption that at very low levels of LCB, the branched polymer is essentially linear; that is, parameter g in the Zimm–Stockmayer relationship[31] is equal to 1. The LCBI relates LCB to the amplification in η_0 due to long branches. The LCBI is given as follows:

$$\mathrm{LCBI} = \left(\frac{\eta_0^{1/a_3}}{[\eta]}\right) k_3^{-1/a_3} - 1 \tag{9}$$

Constants k_3 and a_3 are obtained by the fitting of an equation of the following type:[46]

$$\eta_0 = k_3[\eta]_{\mathrm{L}}^{a_3} \tag{10}$$

where $[\eta]_{\mathrm{L}}$ is the intrinsic viscosity of a linear polymer. The first term on the right-hand side of eq 9 is the viscosity enhancement factor due to LCB. LCBI is 0 for a linear polymer, but there is no way of estimating the LCB content quantitatively as no correlation was provided by Shroff and Mavridis.[46]

Wood-Adams and Dealy[63] proposed a technique of obtaining the MWD from complex viscosity data and called it the viscosity MWD. In this technique, the

Table 3. Correction Values for Branched Polymers[a]

	Shift (ppm)
3° (2°)	−2.65
2° (3°)	−2.45
1° (3°)	−1.40

[a] The values were taken from ref. 42.

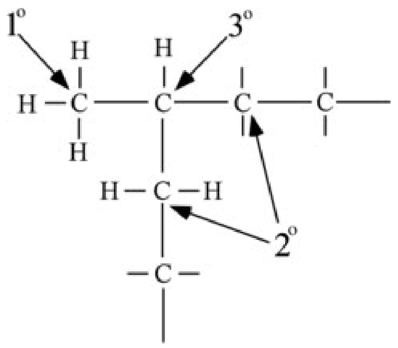


Figure 4. Schematic representation of tertiary, secondary, and primary C atoms.

weight fraction as a function of reduced molecular weight *m* ($m = M/M_w$, where M_w is the weight-average molecular weight) is plotted against *m* to get the MWD. They observed that LCB caused departures in the viscosity MWD in comparison with MWD obtained from GPC measurements.[45] They proposed a routine for quantifying LCB based on this observation with a factor called the peak ratio (PR), which is the ratio of the *m* values of the peaks in the distributions obtained by the two techniques:[45]

$$\text{PR} = \text{GPC MWD peak}/\text{Viscosity MWD peak} \tag{11}$$

Figure 5 shows such a deviation in the peaks of the MWDs obtained with the two techniques.[45] The LCB content for the polyethylene sample shown in Figure 5 was estimated to be $0.8/10^4$ C by NMR.

Wood-Adams and Dealy[45] obtained a correlation between the shift values and the branch content from NMR measurements:

$$\begin{aligned} &\text{LCB}/10^4C = 0 \text{ for PR } \leq 1 \\ &\text{LCB}/10^4C = 1.125 \ \log \ \text{PR for PR } \leq 1 \end{aligned} \tag{12}$$

The reason for employing rheological measurements to estimate the branch content was to overcome the shortcomings of other techniques (solution viscometry, SEC, and NMR) in detecting very low levels of LCB.[64] This puts into doubt the validity of the correlation given by eq 12, which was developed from comparisons with NMR data, especially because of the inability of NMR to differentiate between long branches greater than six carbon atoms in length.[34,42]

The determination of the branch content with dynamic rheology has its share of experimental drawbacks. The frequency limitations of most dynamic rheometers mean that dynamic measurements cannot be carried out in the frequency range of interest. This means that data must be extrapolated by means of viscosity models or with the time–temperature superposition. Simple viscosity models cannot appreciate the rheological complexities of a long-chain-branched structure. Second, LCB is a thermorheologically complex structure,[65] and this means that the simple time–temperature superposition principle is not valid.

QUANTIFICATION OF BRANCHING BY IMAGING TECHNIQUES FOR CARBON AND CERAMIC AGGREGATES

Imaging techniques[66,67] have been employed in the determination of the fractal dimensions, degree of aggregation, and branching of diffusion- and reaction-limited ceramic aggregates. They provide an effective tool for estimating such parameters but suffer the drawbacks of any two-dimensional (2D) imaging technique such as TEM and optical microscopy in describing three-dimensional structures. This is important when we deal with reaction-limited aggregates for which d_f exceeds 2.[67] This can be summarized as follows. Consider that the fractal dimension of the object is d_f and the dimension measured by a 2D imaging technique is d_i:

$$\begin{aligned} d_i &= d_f \text{ for } d_f \prec 2 \\ d_i &= 2 \text{ for } d_f \succ 2 \end{aligned} \tag{13}$$

Branching is observed in aggregates with d_f greater than 2, and 2D imaging techniques would generally be inadequate to quantify these structures (eq 13).

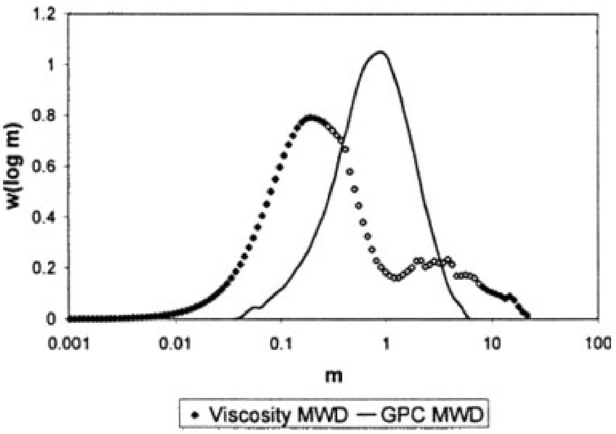


Figure 5. MWD obtained from viscosity and GPC measurements from the work of Wood-Adams and Dealy.[45] Reprinted with permission from Wood-Adams, P. M.; Dealy, J. M. Macromolecules, 33, 7481, 2000. Copyright 2000 American Chemical Society.

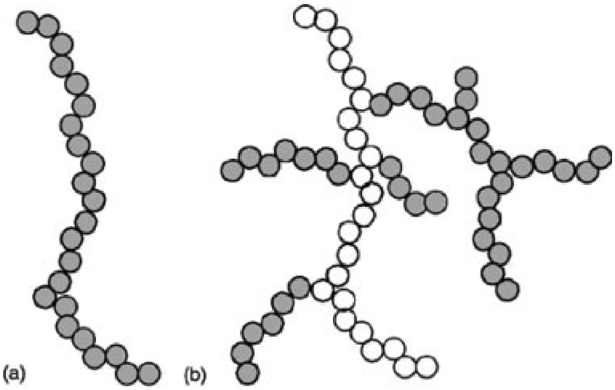


Figure 6. (a) Linear aggregate and (b) branched aggregate composed of primary particles. The open circles represent p through an aggregate.[19] Reprinted with permission from Beaucage, G. Phys Rev E, 70, 031401, 2004. Copyright 2004 by the American Physical Society.

QUANTIFICATION OF THE BRANCH CONTENT BY SMALL-ANGLE SCATTERING

There are local scattering laws such as Guinier's law:[19,68,69]

$$I(q) = G \exp\left(\frac{-q^2 R_g^2}{3}\right) \tag{14}$$

where $I(q)$ is the scattered intensity, q is equal to $4\pi\sin(\theta/2)/\lambda$ (where θ is the scattering angle and λ is the wavelength of radiation), R_g^2 is the coil or aggregate radius of gyration, and G is defined as $N_p n_p^2$ (where N_p is the number of polymer coils in a given volume and n_p is a contrast factor equal to the electron density difference between the polymer coil and the solvent for X-ray scattering). There is also the power law:[19,68,69]

$$I(q) = B_f q^{-d_f} \tag{15}$$

where B_f is the power-law prefactor. These laws give an account of local features such as the size and surface/mass scaling. They cannot independently describe structural features such as branching.[19] However, combining information from such laws can give insight into additional structural information. Beaucage[19] reported a new approach to quantify the branch content by considering aggregates formed from smaller primary particles. Such a description can be considered to be applicable to polymeric and ceramic aggregates (e.g., by considering the primary particles to be the Kuhn step in polymers or the smallest individual particle in a ceramic aggregate). Furthermore, such a structure could be considered to be linear or branched, as shown in Figure 6.[19] The open circles in Figure 6(b) represent the minimum path (p) through the aggregate. A scaling relationship between the degree of aggregation (z), p, and the overall structural size (R_2) and size of the primary particle (R_1) can be given as follows:[18,19,70,71]

$$p^c = z = \left(\frac{R_2}{R_1}\right)^{d_f} \tag{16}$$

where c is known as the connectivity dimension, which is equal to 1 for a linear chain and d_f for regular objects (rod, disk, or sphere). A second scaling relationship between these terms can be expressed in terms of the minimum dimension $d_{\min}$:[18,70]

$$\begin{aligned} p &= \left(\frac{R_2}{R_1}\right)^{d_{\min}} \\ c &= \frac{d_f}{d_{\min}} \end{aligned} \tag{17}$$

where $d_{\min}$ represents the mass fractal dimension of the minimum path [Fig. 6(b)].

Beaucage[19] showed that one could obtain the branch content from eqs 16 and 17 as follows:

$$\varphi_{br} = \frac{z-p}{p} = 1 - z^{(1/c)-1} = 1 - \left(\frac{R_2}{R_1}\right)^{d_{\min}-d_f} \tag{18}$$

The parameter $d_{\min}$ can be calculated from the modified power-law-prefactor equation to account for branched structures:[19]

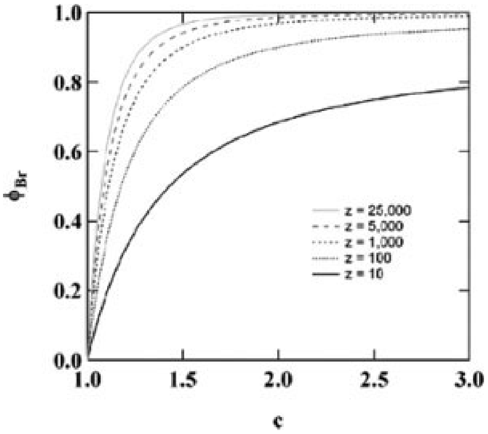


Figure 7. ϕ_{br} as a function of z and c.[19] The figure shows an estimate of the optimum range for the branch content determination. Reprinted with permission from Beaucage, G. Phys Rev E, 70, 031401, 2004. Copyright 2004 by the American Physical Society.

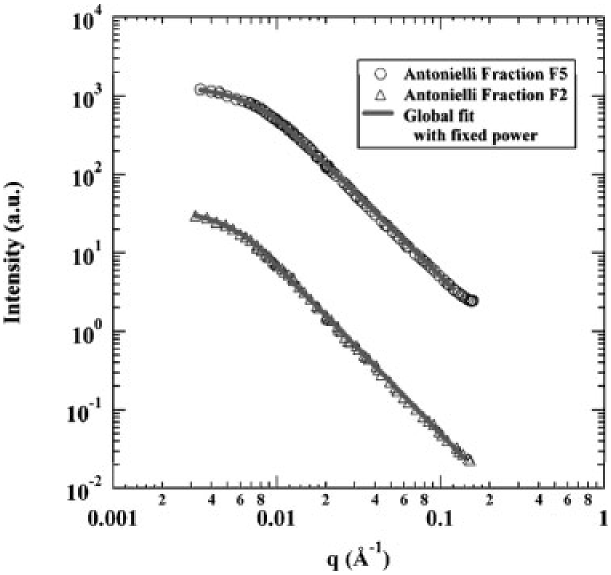


Figure 8. Neutron scattering data from branched polystyrene fit to the unified equation.[19] Reprinted with permission from Beaucage, G. Phys Rev E, 70, 031401, 2004. Copyright 2004 by the American Physical Society.

$$B_f = \frac{G_2 d_{\min}}{R_{g2}^{d_f}} \Gamma\left(\frac{d_f}{2}\right) \qquad (19)$$

where G_2 is the Guinier prefactor for the aggregate, R_{g2} is the aggregate radius of gyration, and d_f is the mass fractal dimension. Because all parameters in eq 17, except $d_{\min}$, are determined with eqs 14 and 15, eq 19 can yield $d_{\min}$, c (eq 17), and ϕ_{br} (because $z = G_2/G_1$, where the subscripts 1 and 2 refer to the primary and aggregate structures fit with eq 14). Figure 7[19] shows the sensitivity of the branch content calculated from such a measurement. This estimation should be good in the range of interest for most commercial long-chain-branched polymers (low c and high z) as well as ceramic aggregates.

Beaucage[19] showed that it could be possible to get branching information for polymers with this approach. In Figure 8, in which neutron scattering data for branched polystyrene are fit to the unified equation,[19,69,71–73] it is shown that it is possible to calculate the parameters $d_{\min}$ and c from such a fit.[19] These model branched polystyrene samples were synthesized with divinyl benzene (10%) as a comonomer to obtain controlled levels of branching but random placement.[74]

ϕ_{br}, obtained from eq 18, gives an average measure of the volume occupied by branches, but it lacks information about the number of branch sites in the aggregate. Thus, it is necessary to complement scattering measurements with other techniques, such as NMR (for polymers) and TEM (for ceramic aggregates), to get a complete picture of branching.

Scattering also offers the potential to describe the distribution of branch lengths through recent applications of techniques such as the maximum entropy method.[71,75–82]

CONCLUSIONS

The quantification of branching in disordered materials remains an active area of research despite several decades of work. Branching is common to both thermodynamically equilibrated structures such as polymers and kinetically determined structures such as ceramic aggregates. In polymers, chromatography, rheology, and spectroscopy have been applied with some success to describe branching, although routine quantification remains allusive. Branching in ceramic and carbon aggregates has been only rarely quantified with microscopy, although theoretical studies indicate the importance of branching to the understanding of physical properties. Recent advances of the application of scattering as a tool to characterize branching in both polymers and aggregates have been discussed. Coupling NMR and scattering techniques to estimate branching in polymers could provide the most comprehensive branch content determination for a broad range of branched systems.

REFERENCES AND NOTES

1. Mandelkern, L. Crystallization of Polymers, 2nd ed.; Cambridge University Press: New York, 2002.
2. Alamo, R. G.; Graessley, W. W.; Krishnamoorti, R.; Lohse, D. J.; Londono, J. D.; Mandelkern, L.; Stehling, F. C.; Wignall, G. D. Macromolecules 1997, 30, 561.
3. Zhang, X. B.; Li, Z. S.; Yang, H.; Sun, C. C. Macromolecules 2004, 37, 7393.
4. Barham, P. J.; Hill, M. J.; Keller, A.; Rosney, C. C. A. J Mater Sci Lett 1988, 7, 1271.
5. (a) Hill, M. J.; Barham, P. J.; Keller, A.; Rosney, C. C. A. Polymer 1991, 32, 1384; (b) Hill, M. J.; Barham, P. J.; Keller, A.; Rosney, C. C. A. Polymer 1991, 32, 84.
6. Hill, M. J.; Barham, P. J.; Keller, A. Polymer 1992, 33, 2530.
7. Wignall, G. D.; Londono, J. D.; Alamo, R. G.; Mandelkern, L.; Stehling, F. C. Macromolecules 1996, 29, 5332.
8. Mirabella, F. M.; Ford, E. A. J Polym Sci Part B: Polym Phys 1987, 25, 777.
9. Mirabella, F. M.; Westphal, S. P.; Fernando, P. L.; Ford, E. A.; Williams, J. G. J Polym Sci Part B: Polym Phys 1995, 26, 1995.

10. Nesarikar, A.; Crist, B. J Polym Sci Part B: Polym Phys 1994, 32, 641.
11. Stephens, C. H.; Hiltner, A.; Baer, E. Macromolecules 2003, 36, 2733.
12. Kulkarni, A. S.; Beaucage, G. Polymer 2005, 46, 4454.
13. Kohls, D. J.; Beaucage, G. Curr Opin Solid State Mater Sci 2002, 6, 183.
14. Medalia, A. I. Rubber Chem Technol 1987, 60, 45.
15. Polmanteer, K. E.; Lentz, C. W. Rubber Chem Technol 1975, 48, 795.
16. Medalia, A. I. J Colloid Sci 1970, 32, 115.
17. Gruber, T.; Zerda, T.; Gerspacher, M. Rubber Chem Technol 1994, 67, 280.
18. Witten, T. A.; Rubinstein, M.; Colby, R. H. J Phys II 1993, 3, 367.
19. Beaucage, G. Phys Rev E 2004, 70, 031401.
20. Lohse, D. J.; Milner, S. T.; Fetters, L. J.; Xenidou, M.; Hadjichristidis, N.; Mendelson, R. A.; Garcia-Franco, C. A.; Lyon, M. K. Macromolecules 2002, 35, 3066.
21. Vega, J.; Aguilar, M.; Peon, J.; Pastor, D.; Martinez-Salazar, J. e-Polymers 2002, 046, 1.
22. Jordan, E. A.; Donald, A. M.; Fetters, L. J.; Klein, L. J. Polym Prepr (Am Chem Soc Div Polym Chem) 1989, 30, 63.
23. Gell, C. B.; Graessley, W. W.; Efstratiadis, V.; Pitsikalis, M.; Hadjichristidis, N. J Polym Sci Part B: Polym Phys 1997, 35, 1943.
24. Kasehagen, L. J.; Macosko, C. W.; Trowbridge, D.; Magnus, F. J Rheol 1996, 40, 689.
25. Wood-Adams, P. M.; Dealy, J. M.; deGroot, A. W.; Redwine, O. D. Macromolecules 2000, 33, 7489.
26. Brinker, C. J.; Scherer, G. W. Sol–Gel Science; Academic: New York, 1990.
27. Agarwal, R.; Horsk, J.; Stejskal, J.; Quadrat, O.; Kratochvil, P. J Appl Polym Sci 1983, 28, 3453.
28. Drott, E. E.; Mendelson, R. A. J Polym Sci Part A-2: Polym Phys 1970, 8, 1361.
29. Mirabella, F. M.; Wild, L. In Polymer Characterization: Physical Property, Spectroscopic, and Chromatographic Methods; Craver, C. D.; Provder, T., Eds.; Advances in Chemistry Series 227; American Chemical Society: Washington, DC, 1990; pp 23–44.
30. Rudin, A. In Modern Methods of Polymer Characterization; Barth, H. G.; Mays, J. W., Eds.; Wiley: New York, 1991; pp 103–112.
31. Zimm, B. H.; Stockmayer, W. H. J Chem Phys 1949, 17, 1301.
32. Beer, F.; Capaccio, G.; Rose, L. J. J Appl Polym Sci 1999, 73, 2807.
33. Graessley, W. W. Polymeric Liquids & Networks: Structure and Properties; Taylor & Francis: New York, 2004.
34. Bovey, F. A.; Mirau, P. A. NMR of Polymers; Academic: New York, 1996; pp 199–203.
35. Yan, D.; Wang, W. J.; Zhu, S. Polymer 1999, 40, 1737.
36. Pollard, M.; Klimke, K.; Graf, R.; Spiess, H. W.; Wilhelm, M. Macromolecules 2004, 37, 813.
37. Kurkiewicz, A.; Eilerts, N. W.; Hsieh, E. T. Macromolecules 1999, 32, 5471.
38. Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. Macromolecules 2000, 33, 6945.
39. Bovey, F. A. Pure Appl Chem 1982, 54, 559.
40. George, M. H.; Grisenthwaite, R. J.; Hunter, R. F. Chem Ind 1958, 1114.
41. Starns, W. H.; Schilling, F. C.; Abbas, K. B.; Plitz, I. M.; Hartless, R. L.; Bovey, F. A. Macromolecules 1979, 12, 13.
42. Randall, J. C. Polymer Sequence Determination: Carbon-13 NMR Method; Academic: New York, 1977; pp 12–17.
43. Randall, J. C. J Polym Sci Polym Phys Ed 1975, 13, 901.
44. Liu, W.; Ray, D. G., III; Rinaldi, P. L. Macromolecules 1999, 32, 3817.
45. Wood-Adams, P. M.; Dealy, J. M. Macromolecules 2000, 33, 7481.
46. Shroff, R. N.; Mavridis, H. Macromolecules 1999, 32, 8454.
47. Hogan, J. P.; Levett, C. T.; Werkman, R. T. Society of Plastics Engineers Journal 1967, 23, 87.
48. Bersted, B. H.; Lee, J. D.; Richter, C. A. J Appl Polym Sci 1981, 26, 1001.
49. Crosby, B. J.; Mangnus, M.; de Groot, W.; Daniels, R.; McLeish, T. C. B. J Rheol 2002, 46, 401.
50. McLeish, T. C. B.; Milner, S. T. Advances in Polymer Science 143; Springer: Berlin, 1999; pp 197–256.
51. Robertson, C. G.; Garcia-Franco, C. A.; Srinivas, S. J Polym Sci Part B: Polym Phys 2004, 42, 1671.
52. Vega, J. F.; Fernandez, M.; Santamaria, A.; Munoz-Escalona, A.; Lafuente, P. Macromol Chem Phys 1999, 200, 2257.
53. Lai, S.; Knight, G. W. Soc Plast Eng Annu Tech Conf Tech Pap 1993, 39, 1118.
54. Kim, Y. S.; Chung, C. I.; Lai, S. Y.; Hyun, K. S. Soc Plast Eng Annu Tech Conf Tech Pap 1995, 41, 1122.
55. Kim, Y. S.; Chung, C. I.; Lai, S. Y.; Hyun, K. S. J Appl Polym Sci 1996, 59, 125.
56. Kim, Y. S.; Chung, C. I.; Lai, S. Y.; Hyun, K. S. Korean J Chem Eng 1996, 13, 294.
57. Vega, J. F.; Munoz-Escalona, A.; Santamaria, A.; Munoz, M. E.; Lafuente, P. Macromolecules 1996, 29, 960.
58. Vega, J. F.; Santamaria, A.; Munoz-Escalona, A.; Lafuente, P. Macromolecules 1998, 31, 3639.
59. Hatzikiriakos, S. G.; Kazatchkov, I. B.; Vlassopoulos, D. J Rheol 1997, 41, 1299.
60. Malmberg, A.; Grabiel, C.; Strffl, T.; Munstedt, H.; Lofgren, B. Macromolecules 2002, 35, 1038.
61. Lai, S. Y.; Plumley, T. A.; Butler, T. I.; Knight, G. W.; Kao, C. I. Soc Plast Eng Annu Tech Conf Technol Pap 1994, 40, 1814.

62. Shroff, R.; Mavridis, H. J Appl Polym Sci 1995, 57, 1605.
63. Wood-Adams, P. M.; Dealy, J. M. J Rheol 1996, 40, 761.
64. Janzen, J.; Colby, R. H. J Mol Struct 1999, 485, 569.
65. Wood-Adams, P. M.; Costeux, S. Macromolecules 2001, 34, 6281.
66. Bushell, G. C.; Yan, Y. D.; Woodfield, D.; Raper, J.; Amal, R. Adv Colloid Interface Sci 2002, 95, 1–50.
67. Tence, M.; Chevalier, J. P.; Jullien, R. J Phys 1986, 47, 1989–1998.
68. Roe, R. J. Methods of X-Ray and Neutron Scattering in Polymer Science; Oxford University Press: New York, 2000.
69. Beaucage, G. J Appl Crystallogr 1995, 28, 717–728.
70. Meakin, P. Prog Solid State Chem 1990, 20, 135–233.
71. Beaucage, G.; Kammler, H. K.; Paratsinis, S. E. J Appl Crystallogr 2004, 37, 523–535.
72. Beaucage, G. J Appl Crystallogr 1996, 29, 134–146.
73. Beaucage, G.; Rane, S.; Sukumaran, S.; Satkowski, M. M.; Schechtman, L. A.; Doi, Y. Macromolecules 1997, 30, 4158–4162.
74. Antonietti, M.; Rosenauer, C. Macromolecules 1991, 24, 3434.
75. Skilling, J.; Bryan, R. K. Mon Not R Astron Soc 1984, 211, 111.
76. Ilavsky, J. Particle Size Distribution from USAXS: A Manual for USAXS Analysis; UNICAT: Argonne, IL, 2000. http://www.uni.aps.anl.gov/~ilavsky. Accessed October 14, 2004.
77. Jemian, P. R.; Weertman, J. R.; Long, G. G.; Spal, R. D. Acta Metall Mater 1991, 39, 2477.
78. Boukari, H.; Long, G. G.; Harris, M. T. J Colloid Interface Sci 2000, 229, 129.
79. Hansen, S. Acta Crystallogr Sect A 1994, 50, 547.
80. Morrison, J. D.; Corcoran, J. D.; Lewis, K. E. J Appl Crystallogr 1992, 25, 504.
81. Potton, J. A.; Daniel, G. J.; Rainford, B. D. J Appl Crystallogr 1988, 21, 663.
82. Tagliani, A. Appl Math Comput 2000, 112, 333.