Analysis of Branched Polymers by High Resolution Multidetector Size Exclusion Chromatography: Separation of the Effects of Branching and Molecular Weight Distribution

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ABSTRACT: This article presents the SEC analysis of branched polyisobutylene PIB and polystyrene PS with high molecular weight and broad multimodal molecular weight distribution. Both polymers were synthesized using an inimer technique, which results in long-chain branched polymers with statistical branching and broad multimodal distributions. Using high resolution multidetector Size Exclusion Chromatography SEC the polymers were analyzed based on three branching factors: \( g = \frac{<R_g^2>_{z,br}}{<R_g^2>_{z,lin}} \), \( h = \frac{<R_h>_{z,br}}{<R_h>_{z,lin}} \), and \( \rho = <R_g^{1/2}>_{z,br}/<R_h>_{z,lin} \). It is generally accepted that for monodisperse branched polymers \( g \) and \( h < 1 \). In the case of our polydisperse PIB and PS, it was seen that \( g \) and \( h > 1 \), and \( \rho \) increases with molar mass and the number of chain ends as predicted earlier. The multidetector SEC system allowed for the separation of branching and polydispersity, reported here for the first time experimentally. The \( g \) parameter as a function of DP, was compared to the theory developed by Zimm and Stockmayer. The plots followed a similar trend, but were shifted by a factor related to the average chain length between branching points. The \( \rho \) parameter decreased with increasing DP, as predicted theoretically by Kajiwara. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 70–79, 2012

KEYWORDS: arborescent polymers; branching characterization; branched polymers; cationic polymerization; gel permeation chromatography (GPC); inimer polymerizations; living carbocationic polymerization; living polymerization; reversible addition-fragmentation chain transfer (RAFT) polymerization; size exclusion chromatography (SEC)

INTRODUCTION Branched polymers are of considerable interest to both academic researchers and industry, due to the unique combination of properties in comparison to their linear counterparts. However, the analysis of branching remains a challenge. Most often the viscosity ratio \( g' \) (eq 1)

\[ g' = \frac{\eta_{w,br}}{\eta_{w,lin}} \]

is used to characterize branching; \( g' < 1 \) indicates contraction of the macromolecular size.

Burchard, Schmidt and Stockmayer2 discussed the analysis of branched polymers using static and quasi-elastic light scattering (LS and QELS). Using the mean-square radius of gyration \( <R_g^2> \), the particle scattering function \( P_z \), and the hydrodynamic radius \( <R_h> \) obtained from the \( z \)-average of the translational diffusion constant \( D_z \) using the Stokes-Einstein equation, they identified four parameters, \( g \), \( h \), \( \rho \), and \( C \), shown in eqs 2–5.

\[ g = \frac{<R_g^2>_{z,br}}{<R_g^2>_{z,lin}} \]
\[ h = \frac{<R_h>_{z,br}}{<R_h>_{z,lin}} \]
\[ \rho = <R_g^{1/2}>_{z,br}/<R_h>_{z,lin} \]
\[ \Gamma = q^2D_z(1 + Cq^2 - ...) \]

Comparing these gave insight into polymer architectures. The authors computed the ratios at the same weight-average molecular weight, because this is directly measured by light scattering. It was pointed out that the difference between \( g \) (radius at the same \( z \)-average molecular weight) and \( g' \) can be substantial for highly polydisperse samples.3 Figure 1 shows the dependence of \( g \), \( h \), and \( \rho \) as a function of \( f \), which refers to the number of chain ends, computed for select structural models.

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The authors stated that in randomly branched polymers and hyperbranched polycondensates $g$ and $h$ are larger than unity for low branching densities, and that they increase with the number of chain ends, in contrast to the decrease observed for stars. They also stated that the reason for this behavior is that polydispersity causes a larger increase of the $z$-average mean-square radius of gyration than the corresponding increase of the weight-average molecular weight. Thus $g$ and $h$ are affected by two effects with opposite consequences: polydispersity, which causes an increase, and branching, which causes the familiar decrease. The authors also pointed out that $g > 2$ and $h > 1$ would clearly indicate random branching.

We analyzed high molecular weight arborescent polyisobutenes (arbPIBS), having long chain branching similar to a tree (branches on branches) with polydispersities ranging from $M_w/M_n \sim 1.5–5$, with our unique high resolution size exclusion chromatography (SEC) system equipped with six Styragel® columns and 5 detectors. arbPIB made by inimer-type living carbocationic polymerization is an ideal system to study branching since the aromatic branch points can selectively be cleaved without affecting the PIB chains as shown in Scheme 1.

$B$ is defined in this manuscript as the average number of branches per molecule. There are different methods of determining $B$. $B_{LD}$ ($B$ from link destruction) is determined experimentally as the ratio of the $M_n$ of the arbPIB and the $M_n$ of the arms (final product after the link destruction reaction; Scheme 1), as shown in eq 6.

$$B_{LD} = \frac{M^{\text{total}}_n}{M_{\text{arms}}^n}$$

Good agreement was found between experimental $B_{LD}$ values and the estimated $B_{\text{kin}}$ (branching based on kinetics) from eq 7.

$$B_{\text{kin}} = \frac{M_n}{C_0^n}$$

$B_{LD}$ corresponds to the dendritic units (D) in the definition of the degree of branching by Fréchet $DB = (T+D)/DP_n$, where $T$ denotes the terminal units in the branched system. For the arbPIB, $D$ is equal to $B_{LD}$. If we consider the initiating and terminating ends of the chain, then $T = B_{LD} + 2$. Using Fréchet’s designations where $DB = (T+D)/DP_n$, then $DB = (2B_{LD}+2) / DP_n$ for the arbPIB.

The equation published later by Simon and Müller et al. is equivalent to $1/B_{\text{kin}}$ in eq 7. The average number of chain

**FIGURE 1** Dependence of $g$, $\rho$, and $h$ on $f$.

**SCHEME 1** Aromatic link destruction method.
ends \( f \) (\( T \) above) was then calculated as \( B + 2 \). We measured the \( R_g \) and \( R_{h,y} \) of linear PIB standards with low polydispersities, constructed radii – \( M_w \) plots, and computed \( g \), \( h \), and \( \rho \) for the \( \text{arbPIB} \) samples.\(^5,11–13\) The plots of \( g \), \( h \), and \( \rho \) against \( f \), calculated as \( B + 2 \), are shown in Figure 2.

It is evident that all parameters are higher than unity. It can also be seen that \( g \) and \( h \) increase with \( f \), with \( g \) reaching values \( >2 \), while \( \rho \) is essentially independent of \( f \). These trends are very similar to those predicted by Burchard et al for polycondensates and randomly branched polymers.\(^2\)

We recently had success in extending the inimer concept to Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization.\(^14\) High molecular weight arborescent polystyrenes (arb\( \text{PS} \)) were synthesized via inimer-type RAFT polymerization of styrene mediated by 4-vinylbenzyl dithiobenzoate (VBThB, inimer) in bulk at 110 °C. The inimer, VBThB, contains both a polymerizable double bond and the characteristic dithioester moiety of a chain transfer agent (CTA). The fragmentation of the VBThB results in the formation of an active radical which can initiate polymerization. The synthesis and structure are shown in Scheme 2.

It should be noted again that in principle inimer polymerizations lead to simultaneous chain growth and branching, resulting in multiple distributions of branched molecules, with more branches in the high molecular weight fractions. Thus \( \text{arbPIB} \) and \( \text{arbPS} \) are expected to have similar architectures. Unfortunately, the selective link destruction technique used in the analysis of \( \text{arbPIB} \) cannot be extended to \( \text{arbPS} \) made by RAFT (Scheme 2). This renders branching characterization very difficult.

In this work, we present the comparative architectural analysis of \( \text{arbPS} \) and \( \text{arbPIB} \)s using high resolution multidetector SEC (refractive index (RI), multiangle light scattering (MALS), quasi-elastic light scattering (QELS) and viscometry (VIS) detectors). This system allowed us to separate the effects of branching and molecular weight distribution experimentally for the first time. The analysis to be presented is generally applicable to randomly branched polymers.

**RESULTS AND DISCUSSION**

**Branching Analysis by Multidetector SEC**

**Branching Parameters**

The SEC system used in this research has six columns, with excellent resolution. Bulk (Mooney) viscosity data were successfully correlated with MW data using six columns, which was not possible with two mixed columns.\(^12\) The presence of five different detectors allowed us to determine different parameters related to the size of the polymers. The system has two concentration detectors (RI and UV, the latter to observe the distribution of groups that absorb UV light). The RI signal is directly proportional to sample concentration, while the UV signal is directly proportional to the concentration of species that absorb UV light at the set frequency. Since the aromatic group from the inimer in \( \text{arbPIB} \) has an absorbance peak around 254 nm, the UV detector set at this wavelength can be used to determine the distribution of inimer in \( \text{arbPIB} \). Figure 3 shows representative multidetector SEC traces of \( \text{arbPIB} \) and \( \text{arbPS} \) listed in Table 1.

The multiangle light scattering detector readily provides absolute molecular weight (\( M_w \)) and radius of gyration (\( R_{g,z} \)) data. The integrated \( R_{g,z} \) is expected to be equivalent with \( R_g \) measured by static light scattering. This detector is essential for branched polymers, since calibration curves are
unavailable for MW determination. Also, a further complexity is introduced if branching is not uniform.\textsuperscript{15} A limitation of R\textsubscript{g,z} measurements is that it can only be measured accurately above 10 nm because the angular dependence of scattered light is too small below this limit. The viscosity detector allows the determination of the hydrodynamic radius (R\textsubscript{h},\textsubscript{g}) and the dilute solution viscosity (\eta\textsubscript{w}) of the polymer, which are useful parameters for branching analysis. The last detector, dynamic or quasi-elastic light scattering detector (QELS) yields R\textsubscript{h} data derived from the diffusion coefficient and includes only the translational Brownian motion. The corresponding radius derived from the intrinsic viscosity, R\textsubscript{h,h}, differs somewhat since the viscosity arises from shear and thus includes irregular rotation. The difference is not large, but according to separate LS measurements by Burchard et al.,\textsuperscript{16,17} R\textsubscript{h} and R\textsubscript{h,h} differ systematically for various architectures. The authors found that R\textsubscript{h,h} and radii obtained from second virial coefficient measurements (R\textsubscript{A2}) agreed very well, but there was no universal relationship among the various radii. Our high resolution SEC-viscometry and SEC-QELS yielded the same R\textsubscript{h,z} within experimental error.\textsuperscript{13} Since SEC-viscometry was found to yield more precise data, thus R\textsubscript{h,z} from viscometry, denoted R\textsubscript{h,h}, is listed in Table 1.

Data from the high resolution SEC system was used to obtain parameters which provide insight into polymer architectures. The SEC system used provides a way to readily determine z-average g, h, g', and \rho branching parameters shown in eqs 1–4. To employ the Burchard method, accurate data for linear monodisperse PS and PIB were needed. The first step was analyzing linear PS and PIB standards with M\textsubscript{w}/M\textsubscript{n} < 1.1 to verify the accuracy of the system and the method employed using this high resolution SEC system.

**SEC Analysis of Linear Polystyrene Standards**

From the values obtained from LS for the linear PS standards (PS30K, PS100K, PS200K, PS400K, and PS925K in Appendix A), a conformation plot of R\textsubscript{g,z} versus M\textsubscript{w} was produced. The conformation plot, shown in Figure 4, is in good agreement with literature data (Podzimek,\textsuperscript{18} Mays et al.,\textsuperscript{19} and Fetters\textsuperscript{20}). Based on the data, eq 8 was produced using a linear fit and was used to compute R\textsubscript{g} for linear, monodisperse PS.

\[
R_g = 1.47 \times 10^{-2} \times M_w^{0.579} 
\]

These data indicate very good solution behavior close to the exponent of \nu = 0.588 predicted by renormalization group (RG) theory.\textsuperscript{18,21}

Similarly, an R\textsubscript{h,h} conformation plot was obtained with the PS standards which also matched well with the literature.\textsuperscript{21} This also agreed well with R\textsubscript{h,i} versus M\textsubscript{i} data obtained from the SEC slices of PS standards. Eq 9 was then used to compute R\textsubscript{h} values for linear monodisperse PS.\textsuperscript{13}

\[
R_h = 47.0 + \frac{66.6}{M_i^{0.76}} 
\]

\[
\eta_w = 129.3 
\]

**TABLE 1 SEC Data of Selected Samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>M\textsubscript{n} (g/mol)</th>
<th>M\textsubscript{w} (g/mol)</th>
<th>M\textsubscript{i} (g/mol)</th>
<th>M\textsubscript{w,forms} (g/mol)</th>
<th>R\textsubscript{h,z} (nm)</th>
<th>R\textsubscript{h,h} (nm)</th>
<th>\eta\textsubscript{w} (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JEP06-190-3 (arbPIB)\textsuperscript{a}</td>
<td>260,400</td>
<td>551,200</td>
<td>1,210,000</td>
<td>93,200</td>
<td>27.9</td>
<td>34.5</td>
<td>96.7</td>
</tr>
<tr>
<td>AH221-5 (arbPS)\textsuperscript{b}</td>
<td>319,800</td>
<td>881,200</td>
<td>3,336,000</td>
<td>–</td>
<td>47.0</td>
<td>66.6</td>
<td>129.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a} [MeOIM]o = 1.14 \times 10^{-3} M; [IB]o = 1.74 M; [IB]/[MeOIM]o = 1526; [TiCl4]o = 3.13 \times 10^{-2} M; Hx/MeCl 60/40 v/v; [D6BP]o = 5.10 \times 10^{-3} M; Temp.: \textquotesingle -95 °C.

\textsuperscript{b} [St]o = 8.73 M; [VBTbH]o = 5.18 \times 10^{-4} M; Temp.: 110 °C.
The Mark-Houwink-Sakurada equation yielded 
\[ K = 1.1 \times 10^{-2} \text{ (mL/g)} \] and 
\[ a = 0.71 \text{ (R}^2 = 0.996) \] which were used to calculate 
ye values for linear monodisperse PS. The exponent predicted by scaling laws 
\[ a = 3v - 1 = 0.704 \] and 
\[ a = 0.728 \] from eqs 8 and 9) is in agreement within 
experimental error with 
\[ a = 0.766 \] from the RG theory.

**SEC Analysis of Linear Polyisobutylene Standards**

For PIB, new conformation plots were determined using 
both nominal \( M_w \) (provided by the manufacturer) and \( M_w \) 
measured by LS for comparison. The PIB standards had 
broad polydispersity than the PS standards (Table 1). Unlike the PS standards, the PIB standards were polydis-
perse, so the \( R_g \) data had to be corrected for this polydispersity using eq 10 developed by Burchard et al.:²

\[
\frac{g_{\text{linear}}}{g_{\text{monodisperse}}} = \frac{m + 2}{m + 1} \\
\frac{1}{m} = (P_w/P_n) - 1
\]

Equation 11 shows the correlation obtained from Figure 5.

\[ R_{h,i} = 1.12 \times 10^{-2} \times M_w^{0.598} \]

Again the \( R_g \) data indicate very good solution behavior close to 
the exponent of \( v = 0.588 \) predicted by renormalization theory.

The \( z \)-average hydrodynamic radii \( R_{h,z} \) versus measured 
\( M_w \) plot of the linear PIB standards is compared to the \( R_{h,i} - M_i \) plot obtained for the individual slices of a series of PIB 
standards in Figure 6. The agreement is quite good. Equation 
12 shows the correlation.

\[ R_{h,i} = 1.64 \times 10^{-2} \times M_w^{0.550} \]

The \( R_{h,z} \) versus \( M_w \) correlation (eq 13) published earlier¹¹ 
was measured using SEC-VIS/RAFS (viscometry/right-angle 
light scattering). Based on the current data, the earlier 
method overestimated the \( R_h \) at the same molecular weight.

\[ R_{h,z} = 2.307 \times 10^{-2} \times M_w^{0.55} \]

The Mark-Houwink-Sakurada equation⁶ yielded 
\[ K = 2.2 \times 10^{-2} \text{ (mL/g)} \] and 
\[ a = 0.667 \], which was used to compute the 
viscosity of linear monodisperse PIB (scaling prediction gives 
a = 0.794).²²

**Integrated Branching Parameters**

The tables in Appendix B and C list integrated branching pa-
rameters calculated for previously published SEC data of
arbPIB$^{5,7,8,13,23,24}$ and arbPS$^{14}$ together with those calculated for the samples listed in Table 1. $g'$ is smaller than unity for all samples, which is indicative of branching. $q$ was calculated directly from $R_{g,z}/R_{h,z}$ given by MALS and VIS, respectively. $g$ and $h$ were determined using the ratio of $R_{g,z}$ and $R_{h,z}$ of the arborescent samples and the $R_{g,i}$ and $R_{h,i}$ of linear monodisperse samples derived from eqs 8–12. Figures 7–9 display plots of the integrated branching parameters against the weight-average degree of polymerization (DP$_w$). For branched polymers with narrow distribution, the values for $g$ and $h$ are expected to be less than unity; however, it can be seen that in the case of broad distribution, the parameters are higher than unity, except for a few cases, where low molecular weight samples of arbPIB display $h < 1$. The reason for this behavior is that the polydispersity of the samples results in a larger relative increase in the mean-squared dimensions than the familiar decrease resulting from the branching$^{4,5}$ Therefore, it was of interest to analyze the branching of these materials in the absence of polydispersity.

Branching Distributions—Analysis of Monodisperse SEC Fractions

To separate the effects of a broad molecular weight distribution and branching, the samples in Appendix B and C were analyzed by high resolution SEC, and the branching parameters were computed for each close to monodisperse slice across the whole distribution using the ASTRA$^9$ software. Using this method, the actual $R_{g,i}$ and $M_i$ values were used instead of the averaged values. Both SEC traces show a broad, multimodal distribution, that is, characteristic of these inimer-type polymerizations. For both polymers, a pronounced, well-separated peak is seen at low molecular weight in the SEC-RI traces, which indicates a high amount of lightly branched molecules.

For all fractions, in Appendix B and C, the measured MW is higher than the theoretical, indicating branching in all fractions. The UV trace of the arbPIB in Figure 3(a) shows that the inimer is distributed throughout the molecular weight distribution, since the inimer absorbs UV light, but PIB does not. In Figure 3(b), the UV and RI traces are very similar as expected, since all the units in arbPS absorb UV light. The molecular weight is measured by light scattering every 0.5 sec on the eluting samples, allowing the determination of the branching parameters at each 0.5 sec interval.

The $R_{g,i}$ and $R_{h,i}$ conformation plots for the arborescent samples are plotted in Figure 10. The plots run parallel, with the arbPS showing much larger $R_{g,i}$ but similar $R_{h,i}$ values at the same $M_i$ compared to arbPIB. The slopes (m) are smaller than those for the corresponding linear polymers which shows that for any given molar mass, the arborescent polymer is more compact, which indicates branching in all fractions.
Using the $R_g$ obtained for each slice of the SEC trace for JEP06-001-4 (arbPIB), values of $B$ were determined using eq 14, which was derived by Burchard and coworkers\textsuperscript{2} for randomly branched polycondensates. In this case $B$ is a function of branching probability and is essentially equal to the branch points per molecule based on the number-average degree of polymerization.

\[
\left( \frac{R_g}{R_h} \right)_{0.1 m} = \frac{6}{B} \left( \frac{2 + B}{B} \right)^{1/2} \ln \left[ \frac{(2 + B)^{1/2} + B^{1/2}}{(2 + B)^{1/2} - B^{1/2}} \right] - 1
\]

The number of chain ends ($f = B + 2$; $f = T$ in Fréchet’s designation\textsuperscript{9}) was then computed and plotted versus molecular weight as seen in Figure 11. A linear increase of the number of chain ends with molecular weight is observed, and the line extrapolates to $f = C_{24}$. In 1949, Zimm and Stockmayer (Z-S) developed equations relating the branching parameter ($g$) for uniform fractions to the average number of branching units per molecule (B) for systems with trifunctional (eq 15) monomers.\textsuperscript{3} In that work, the authors denote the average number of branches with the letter $f$. However, in this article, we have assigned $f$ to be the number of chain ends, which is $f = B + 2$. To simplify things, we will modify the original equations to include the proper term used in this article. This is another case of using a different character to describe the same variable.

\[
\langle g_3(B) \rangle_{N_b} = \left( 1 + \frac{B}{7} \right)^{1/2} \frac{4B}{9\pi}^{-1/2}
\]

For a polycondensation of trifunctional monomers, $DP_i = f = B + 2$. Therefore, eq 15 can be used to determine a relationship between $g$ and $DP_i$ for the Z-S theory. Values of $g$ versus $DP_i$ for the arbPIB (JEP06-090-f) and arbPS (AH22108-5) were determined experimentally from the SEC-MALS. This data is plotted in Figure 12. The plots of the experimental data follow the same general trend as the Z-S relationship, although the power law exponents are lower than the predicted 0.5.

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The arbPIB and arbPS plots were shifted to overlap the theoretical plot. The ratio of $DP_i$ (exp) / $DP_i$ (Z-S) at a given value of $g$ is related to the average chain length between the branching points (branch length) for the arbPIB and arbPS. In an ideal living copolymerization, this length should remain constant throughout the entire distribution of species. This would correspond to an equal reactivity of species and a controlled molecular weight growth with increasing conversion (as per a typical living polymerization). Evidently, a more complex behavior is found as demonstrated in Figure 13. For the arbPIB, at low conversion, the small amount of inimer preferentially incorporates into the polymer and the arm length increases; however, towards the end of the reaction the average chain length decreases because the IB is in
large excess and the inimer is depleted at low conversion. However, the $DP_n$ of the branches is between 400 and 500. The experimental link destruction (see Scheme 1) gave $DP_n = 1660$. The discrepancy between these two values is likely due to chain flexibility and solvent interactions that must be accounted for in the experimental data.

The $arb$PS has fewer and significantly longer arms ($2800 < DP_i < 4000$) with a strong general decrease in arm length at low $B$ followed by a slight increase at high $B$. This shows that in the RAFT polymerization, the styrene units are preferentially consumed during the early part of the reaction, yielding longer chains. We have seen this experimentally in other studies. The larger molecules produced near the middle of the reaction have chains that are on average shorter, indicating branching during the middle part of the reaction, likely in the form of the polymerization of macromonomers containing the vinyl group of the CTA inimer. The branches then continue to grow at the end of the reaction. In general, the PS appears to have fewer highly branched species, which is likely due to the fact that the polymerization cannot proceed to high conversions without undergoing irreversible termination.

Kajiwara theorized the values for $h/g$ (essentially $\rho^{-1}$) (1.3346) for a system of random isomeric branched molecules consisting of all possible monodisperse molecules of $f$ functionality. He also determined that $h/g$ versus $DP_i$ would increase asymptotically and approach a value of 1.3346 at high $DP_i$, so theoretically, $\rho$ should decrease asymptotically to this value. Figure 14 shows the plots of $\rho$ versus $DP_i$ for $arb$PIB and $arb$PS.

The curves show similar behavior but differ in their amplitude. The reason for such behavior is presently not yet known but may be a result of a considerably lower branching density of the $arb$PS sample than observed with the $arb$PIB. The $\rho$ values decrease, and upon reaching appreciable $DP_i$, approach a constant value which appears to be between 1.1 and 1.3, which is close to that predicted by Kajiwara.

Kajiwara also calculated $h$ as a function of $DP_i$ and showed that it continuously decreases to values $\sim 0.2–0.3$ depending on $f$. Figure 15 shows the plots of $h$ versus $DP_i$ (with the fitted power law equation) to give insight into the architecture of these selected $arb$PIB and $arb$PS samples when molecular weight distribution is no longer a consideration (Fig. 15).

**Basis of Theory**

A new preliminary prediction to describe the inimer-type reactions is under development. An outline of the rather complex derivation is beyond the scope of this article. Details will be given in a separate presentation elsewhere. In this manuscript, only a more intuitive explanation is given.

The mentioned prediction will be made on a mean field approach similar to the Stockmayer and Gordon et al. Mean field means here the Flory assumption that any functional group in a polymer has the same reactivity regardless of size and molecular architecture. The main difference between randomly branched and arborescent
structures is that in the former the branched cluster formation is mediated through monomer–monomer reaction. In the inimer/monomer copolymerization, one has a different situation. Once a growing chain, initiated by an inimer, reacts with the double bond of another inimer at the end of a chain, the entire already formed chain becomes attached to the growing chain. This structure now has two actively growing ends (i.e., a bidirectional growth) and can attach to other more or less branched clusters as the reaction progresses. In the case of the RAFT inimer, first linear macromonomers form which contain a vinyl group originating from the VBThB. We have observed this experimentally in another study through MALDI-ToF mass spectrometry. These macromonomers are preferentially consumed during the middle of the reaction which gives branching.

Although the chain growth is a controlled reaction, the copolymerization reaction with an inimer double bond is a random process. As a consequence of directional growth constraint, a less polydisperse structure is obtained than if the process were fully random where such directed flow is neglected; therefore, behavior between fully random and uniform structures is observed. This feature of randomness makes an increase of the \( g \)-branching factor understandable, yet less than in a fully random reaction. Still, a certain memory of the controlled chain reaction remains effective.

The decrease of the contraction factors at high conversion is not easily understood but may strongly depend on the copolymerization parameters. For instance, if the polymerization of the inimer double bond is favored, a more pronounced random branching results at low conversion, connected with a stronger increase of the \( g \)-factor. At higher conversion the isobutylene or styrene monomers predominate and only linear chains will become attached (like in star forming processes); however, this linear growth of side chains is again a controlled reaction leading to a more uniform structure and a decrease of the \( g \) parameter.

**EXPERIMENTAL**

**Materials**

\( \text{Arb} \)PSSs were synthesized as described in the literature using the 4-vinylbenzyl dithiobenzoate (VBThB) CTA-inimer. \( \text{Arb} \)PIBs were synthesized as described using the 4-(2-methoxysopropyl)styrene (MeOIm) inimer. Linear PS and PIB standards were purchased from American Polymer Standards. The data is shown in Appendix A in the Supporting Information.

Size Exclusion Chromatography (SEC) Analysis. Samples were prepared at concentrations of \( \sim 1.0 \) mg/mL in THF and analyzed in THF. The \( dn/dc \) values for PS and PIB were used. Although the incorporation of the inimer will have a different \( dn/dc \) than the monomer, the low concentration will make any change negligible.

The SEC system uses a Waters setup equipped with six Styrage columns (HR0.5, HR1, HR3, HR4, HR5, and HR6), a Wyatt Technology ViscoStar viscometer, a Wyatt Optilab DSP RI detector (thermostatted at 40 °C), Wyatt DAWN EOS 18 angle Multiangle Light Scattering (MALS) detector \( (\lambda = 690 \text{ nm}) \), and a Wyatt Quasielastic Light Scattering QELS detector at a 90° angle. The system is equipped with a continuous, recycling THF distillation with a flow rate of 1 mL/min. The columns are heated at a constant temperature of 35 °C. Absolute molecular weights, radii of gyration, and hydrodynamic radii were determined using ASTRA software version 5.3.2.15.

**CONCLUSIONS**

Branched polyisobutylene PIB and polystyrene PS with high molecular weight and broad multimodal molecular weight distribution were analyzed by high resolution, multi detector SEC based on three branching factors: \( g = \langle |R_z|^2 |z, \text{lin}\rangle M_w/\langle |R_z|^2 |z, \text{br}\rangle M_w \); \( h = \langle |R_0|^2 |z, \text{lin}\rangle M_w/\langle |R_0|^2 |z, \text{br}\rangle M_w \); and \( \rho = \langle |R_z|^2 \rangle^{1/2}/\langle |R_0|^2 \rangle \). It was found that for the unfractionated, polydisperse samples \( g \) and \( h > 1 \) and \( \rho \) ranged from \( \sim 1.0 \) to 2.2. Branching was analyzed separately without the influence of polydispersity by considering each individual SEC fraction to be a distinct monodisperse polymer. In the absence of polydispersity, the branching parameters behaved as predicted for monodisperse branched polymers: \( g \) and \( h < 1 \) and decreased with increasing \( DP_i \) indicating more branching in the higher molecular weight fractions. The \( g \) parameter as a function of \( DP_i \) was compared to the theory developed by Zimm and Stockmayer. The plots followed a similar trend, but were shifted by a factor related to the average chain length between branching points, \( \rho \) also followed theoretically predicted trends. In the case of the polydisperse samples, \( \rho \) remained relatively constant with increasing \( DP_i \) as predicted by Burchard et al. and when the SEC slices were analyzed as monodisperse fractions, \( \rho \) decreased asymptotically to values of approximately 1.1 to 1.3, which is close to that predicted by Kajiwara. A new preliminary prediction based on mean field theory is currently under development to describe the nature of polymers synthesized inimer-type polymerization.
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