Unusual Contributions of Molecular Architecture to Rheology and Flow Birefringence in Hyperbranched Polystyrene Melts

SEMEN B. KHARCHENKO,1 RANGARAMANJAM M. KANNAN,1 JEFF J. CERNOHOUS,2 SHIVSHANKAR VENKATARAMANI,1 GADDAM N. BABU2

1Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan 48202
23M Corporate Research Laboratories, 3M Center, St. Paul, Minnesota 55144-1000

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ABSTRACT: With the increase in sophisticated synthesis methods, it appears that polymer architecture may be a tunable property. Therefore, the role of architecture in rheological and processing properties has received renewed attention, mainly because of dendrimer synthesis and metallocene-catalyst technology. Linear polymers and hyperbranched polymers represent two ends of branching complexity. Some previous studies have suggested that hyperbranched polymers may behave like unentangled polymers, whereas others have proposed that they exhibit the properties of soft colloids. In an effort to compare the responses of linear and hyperbranched polymers, we synthesized starlike hyperbranched polystyrenes (HBPSs) of various branch lengths and numbers of branches. The HBPSs used in this study were unentangled or weakly entangled, allowing us to study the effect of branch density more readily. Two linear polystyrene (L-PS) melts and two HBPSs were studied. Using a custom-built rheooptical apparatus, we characterized the rheology and flow birefringence of these materials. To our knowledge, these are the first flow birefringence measurements on highly branched polymer melts. Our results suggest that the flow behavior of HBPSs is significantly different from that of L-PS: (1) HBPS shows nonterminal behavior in the low-frequency rheological response; (2) when the stress-optical rule (SOR) holds, the stress-optical coefficient of HBPS is much lower than those of analogous linear polymers; and (3) when the branch density is high and the branch length is sufficiently low, the SOR fails for these homopolymer melts. A significant increase in the birefringence for a given amount of stress in the low-frequency region suggests that there may be a soft core in these materials due to the strong preferential radial orientation of chain segments near the center of a molecule versus those near the periphery. The predominantly elastic response of the soft structures may be responsible for the enhanced form birefringence. Our preliminary results indicate that these materials may exhibit both polymeric and soft-colloid natures. © 2001 John Wiley & Sons, Inc. J Polym Sci Part B: Polym Phys 39: 2562–2571, 2001

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INTRODUCTION

Hyperbranched and dendritic polymers have kindled scientific and technological curiosity because of their flexibility in functionalization and architecture and the novel properties that can potentially be achieved as a result. For example, with the same overall molecular weight a linear polymer has, hyperbranched polymers (HBPs) possess a significantly lower viscosity, thereby allowing greater coating speeds. With improved synthesis methods, properties of HBPs are being tailored through the careful control of the architecture and end-group chemistry. Such modified poly-
mers are already finding applications as potential surface modifiers, tougheners for epoxy composites, and drug- and gene-delivery vehicles. In comparison with dendrimers, which have a well-defined architecture and are monodisperse, HBPs are polydisperse and have an irregular branching structure. The major advantage of HBPs is that they can be synthesized in one step, in contrast to dendrimers, which undergo a relatively expensive multistep synthesis.\textsuperscript{1–4} To take advantage of such novel materials, we need a clear understanding of the effect of the architecture on rheological and processing properties. These issues have received attention only recently, even though star polymers have been a subject of theoretical and experimental investigations for several decades.\textsuperscript{5–13}

The rheological behavior of dendrimers and HBPs is similar to that of Newtonian fluids. The high degree of branching makes it difficult for the molecules to entangle within themselves and with other molecules. Therefore, the rheology appears to reflect an unentangled polymer-like behavior, with the zero-shear viscosity governed by the end-group chemistry and the generation number.\textsuperscript{14–17} However, some studies suggest that the rheology and orientation behavior of hyperstar polymers may also reflect a soft-colloid-like response, with structural contributions becoming significant at long timescales.\textsuperscript{18–20} The potential dual nature of the dynamics and orientation of highly branched polymers is the subject of this article. We seek to address the response of such materials by synthesizing starlike hyperbranched polystyrenes (HBPSs) with controlled branch lengths. These materials reflect the branching complexity of HBPs without the end-group effects. At the same time, the starlike nature allows us to draw parallels with the behavior of symmetric star polymers, which we address in a forthcoming article.\textsuperscript{21} Using quantitative rheological and flow birefringence measurements on these homopolymer melts, we show some peculiar rheoptical responses, which provide a glimpse of the dual nature of HBPSs.

BACKGROUND

The remarkable effect of branching on rheology has been extensively studied, both experimentally and theoretically, in star polymers.\textsuperscript{5–13,18–20,22–24} The most interesting features appear to be (a) the relaxation spectrum broadening, (b) the terminal relaxation time ($\tau_\text{e}$) and viscosity ($\eta$) increasing exponentially with the arm molecular weight ($M_a$), and (c) the dependence of $\tau_\text{e}$ and $\eta$ only on $M_a$ and not on the number of arms ($f$). Therefore, it has been concluded that the complex relaxation of star-branched polymers in the melt occurs via two major motions. The fast mode is attributed to the segmental relaxation, which is independent of $M_a$ and $f$, and the slower mode corresponds to the orientation relaxation of arms and is dependent on $M_a$. The latter represents inherent polymeric character. For entangled star polymers, the branch point suppresses reptation, and the cooperation of all the arms is required for the molecules to relax. The reptation theory has been consequently modified to describe the dynamics of these systems. Milner and McLeish introduced contour-length fluctuations with constraint release and developed a parameter-free theory to describe the relaxation process of branched polymers, in which only two factors were needed to accurately depict the relaxation process of the star: the polymer entanglement molecular weight ($M_e$) and its monomeric friction coefficient ($\xi$).\textsuperscript{11,22–24} The independence of the terminal zone rheology on $f$ is captured by the theory, but the authors suggested that it would be valid only when $f$ is small enough such that the branch point is not overcrowded. When $f$ is large, high branching density near the core may lead to preferential orientation of chains in the radial direction. Rheological response, in this case, is manifested through extra-slow structural relaxation modes, as experimentally observed.\textsuperscript{18–20}

Even though entangled hyperstar polymers and dendritic polymers are spherically shaped molecules, their dynamics and rheological behavior seem to have distinct origins, thereby representing two different classes of branching complexity. Many dendritic polymers and HBPs exhibit Newtonian behavior in simple shear. For higher generation dendrimers, the intrinsic viscosity is a weak function of molecular weight (Mark–Houwink exponent $a \ll 0.5$), suggesting a compact spherical structure, with dense branching near the surface, that prevents molecular interpenetration. The zero-shear viscosity has been found to depend strongly on the terminal functionality, indicating that intermolecular interactions may be playing a strong role in the rheology, rather than entanglement dynamics.\textsuperscript{14–17} The poly(amidoamine) (PAMAM) dendrimers do not show an entanglement plateau or a sudden increase in the zero-shear viscosity beyond a certain molecular weight, as is characteristic of entangled polymers. Therefore, there is little interpenetration between parts of different molecules,
suggesting a structural model of molecules with a softer core and a denser shell. Consequently, the rheology of the dendrimers is dominated more by the end functionality, rather than by the presence or absence of entanglements.

To separate the effect of a high degree of branching from the effect of end functionality, it would be beneficial to have hyperbranched structures with no specific end groups. To achieve this, we synthesized model polystyrene HBPs anionically, with the branch length fixed. The number of branches \( f \) was relatively large; however, the range of branch molecular weights was such that they were either unentangled or weakly entangled. This allowed us to explore the effect of a high degree of branching, where entanglement effects were not significant. Mechanical and flow birefringence responses of these materials were measured quantitatively and simultaneously over a wide range of temperatures and shear frequencies. The measurements reveal unique effects associated with the high degree of branching in these materials.

### MATERIALS

Model hyperbranched polystyrenes (R-HBPs) were synthesized by anionic polymerization, the principles of which are described elsewhere. Living linear polystyrene (L-PS) chains were grown to a desired molecular weight and subsequently treated with pure divinyl benzene (DVB) to induce branching. Five repeat units of DVB were added to the chain end. What ensued was a mixture of propagation and coupling of chains. However, because none of the anions were quenched, the reaction continued until all of the double bonds were consumed. Because the branching agent was added only to one end of the chain, the branch points of the resultant HBPs would be expected to be near the center. Therefore, the HBPs discussed in this study are most likely to be starlike HBPs. Molecular characterization was performed via a Viscotek triple detection system, with gel permeation chromatography (GPC), dynamic light scattering, and intrinsic viscosity measurements. The detailed synthesis, molecular weight, and solution viscosity characterization will be described in greater detail elsewhere.

Compared to the intrinsic viscosities of linear polymers of the same molecular weight, the intrinsic viscosities of HBPs were much smaller (Table I). For this reason, hydrodynamic radii \( R_h \) were evaluated according to

\[
R_h = \frac{3}{2} [\eta] M \left(\frac{10 \pi N_A}{\rho}\right)^{-1/3}
\]

where \( M \) is molecular weight and \( N_A \) is Avogadro's number.

The ratio of \( R_h \) of HBPs to that of L-PS of a corresponding total molecular weight is approximately 0.5. Additionally, the Mark–Houwink exponents \( (a) \) of HBPs were estimated to be less than 0.3. Such significantly lower values of \( a \) and \( R_h \) of high molecular weight HBPs are indicative of their compact configurations. These numbers are comparable to those of dendrimers and randomly hyperbranched polymers in both experiment and simulation, suggesting that our model HBPs can indeed be visualized as nearly spherical, dense molecules.

### Table I. Intrinsic Viscosity Comparison for L-PS and HBPS

<table>
<thead>
<tr>
<th>Polymer Architecture</th>
<th>( M_w ) (g/mol)</th>
<th>( M_n ) (g/mol)</th>
<th>PDI</th>
<th>([\eta]) (dL g(^{-1}))</th>
<th>( R_h ) (nm)</th>
<th>Estimated ( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13K-L-PS</td>
<td>13,502</td>
<td>12,738</td>
<td>1.06</td>
<td>0.096</td>
<td>2.7</td>
<td>—</td>
</tr>
<tr>
<td>171K-L-PS</td>
<td>171,000</td>
<td>164,000</td>
<td>1.04</td>
<td>0.63</td>
<td>11.9</td>
<td>—</td>
</tr>
<tr>
<td>531K-L-PS(^a)</td>
<td>531,000</td>
<td>525,600</td>
<td>1.01</td>
<td>1.33</td>
<td>22.4</td>
<td>—</td>
</tr>
<tr>
<td>121K-L-PS(^a)</td>
<td>1,206,000</td>
<td>118,200</td>
<td>1.02</td>
<td>3.03</td>
<td>38.7</td>
<td>—</td>
</tr>
<tr>
<td>HBPS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10K-R-HBPS</td>
<td>575,600</td>
<td>458,200</td>
<td>1.26</td>
<td>0.13</td>
<td>10.5</td>
<td>50</td>
</tr>
<tr>
<td>50K-R-HBPS</td>
<td>1,264,000</td>
<td>731,000</td>
<td>1.73</td>
<td>0.36</td>
<td>19.4</td>
<td>25</td>
</tr>
</tbody>
</table>

\(^a\) Presented for intrinsic viscosity comparison only.
small amount of polydispersity in \( f \). 10K-R-HBPS and 50K-R-HBPS are estimated to have \( f = 50 \) and \( f = 15 \), respectively.\(^{21}\) \( M_w \) of polystyrene is about 18,100 g/mol;\(^{31}\) therefore, on the basis of the branch molecular weight, 10K-R-HBPS is expected to be unentangled, and 50K-R-HBPS is expected to be weakly entangled. To compare the rheo-optical response of R-HBPS with those of linear polymers, we purchased nearly monodisperse L-PSs of various molecular weights from Scientific Polymer Products, Inc.

The samples to be tested in the RSA-II shear sandwich were prepared via the compression molding of pellets (or powder) at temperatures well above the glass-transition temperature, depending on the molecular weight, with a thermopress obtained from Carver, Inc. Once the desired shape was achieved, the sample was unloaded and cooled to room temperature. To remove any bubbles that may have resulted from the molding, we annealed the samples under vacuum at an elevated temperature (glass-transition temperature + 50 °C). Upon loading in the RSA-II at about 150 °C, any residual orientation caused by the squeezing of the shear sandwich outer plates was allowed to relax completely by the sample being kept at rest for approximately 40 min.

**EXPERIMENTAL**

**Stress-Optical Rule (SOR)**

For homopolymer melts under simple shear flow, the deviatoric parts of the stress tensor (\( \sigma \)) and birefringence tensor (\( n \)) are found to be proportional and coaxial over a wide range of flow conditions. This SOR holds well for homopolymer melts and solutions because both the stress and birefringence arise from the second moment of orientation of chain segments. The proportionality constant is called the stress-optical coefficient (\( C \)) and is observed to be independent of frequency and weakly dependent on temperature. The SOR is given by\(^{32}\)

\[
\sigma = n/C
\]

and:

\[
C = \frac{2\pi \left(n^2 + 2\right)(\alpha_1 - \alpha_2)}{45nkT} \tag{2}
\]

where \( n \) is the mean refractive index and \( T \) is the temperature. Because \( C \) depends on the anisotropic polarizability of the monomer (\( \alpha_1 - \alpha_2 \)), it is expected to be nearly independent of molecular weight and molecular architecture. However, for L-PS, the molecular weight dependence of \( C \) was observed by Kornfield and Verma.\(^{33}\) To our knowledge, it has not been measured previously for star polymers and HBPs.

**Rheo-optical Apparatus**

The rheological and flow birefringence measurements were performed using a custom-built rheo-optical apparatus.\(^{34,35}\) Stress and flow birefringence were measured over a wide range of temperatures (120–230 °C) and oscillatory shear frequencies (100–0.1 rad/s). Stress measurements were carried out in a strain-controlled Rheometric Scientific solids analyzer (RSA-II). The samples were tested in shear sandwich geometry (Fig. 1), which was modified to allow optical measurements in either the shear–shear gradient plane or the shear–vorticity plane. In this work, measurements in the shear–shear gradient plane are reported.

Flow birefringence was measured quantitatively and simultaneously with stress, using the polarization-modulation scheme developed by Fuller et al.\(^{34}\) and the signal analysis scheme analogous to the one developed by Kannan and Kornfield\(^{35}\) (Fig. 2). Monochromatic light coming from the He–Ne laser was initially polarized with a wire-grid polarizer (extinction = 10,000:1). The linearly polarized light was passed through the combination of a photoelastic modulator (PEM) and a quarter wave plate (QWP). The PEM introduced very high frequency retardation (\( f = 41 \) kHz) used to continuously alter the polarization.
state from linear to circular. The light was then sent through a sample undergoing oscillatory shear deformation. To produce optically flat surface, we fixed glass windows to the shear sandwich. After leaving the sample, the beam was sent through a circular polarizer. The intensity was measured with a photodetector and was subsequently demodulated with two lock-in amplifiers: LI-1f, set to a reference frequency \( f = 41 \text{ kHz} \) of the PEM, and LI-2f, set to twice the reference frequency of the PEM \( (2f = 82 \text{ kHz}) \). LI-1f and LI-2f were sensitive to the components of the birefringence that are proportional to shear stress \( \sigma_{12} \) and normal stress \( N_1 \), respectively. A polarizer and a QWP were used for optical train calibration. We measured the reference direct-current intensity \( I_{dc} \) by sending the signal from the detector to a low-pass filter. The strain, stress, and intensity from LI-1f \( (I_{1f}) \), LI-2f \( (I_{2f}) \), and \( I_{dc} \) were acquired and analyzed with LabVIEW. The signals from the lock-in amplifiers were normalized by \( I_{dc} I_{1f} I_{2f} \) and \( I_{dc} I_{2f} \) were used to calculate the magnitude of retardation \( \delta \) and the orientation angle of retardation \( \chi \) with signal analysis developed elsewhere. \( \delta \) is related to birefringence \( (\Delta n') \):

\[
\Delta n' = \delta (\lambda/2\pi d)
\]  

(3)

where \( \lambda = 633 \text{ nm} \) and \( d \) is the path length of light in the shear sandwich. The magnitude and orientation angle of the birefringence and the stress tensor can be related to each other in the shear–shear gradient plane with eq 1, as described below. For small-amplitude oscillatory shear \( (\gamma = \gamma_0 \sin \omega t) \), the shear stress is described by

\[
\sigma_{12} = \gamma_0 (G' \sin \omega t + G'' \cos \omega t)
\]  

(4)

where \( \gamma_0 \) is the strain amplitude; \( \omega \) is the shear frequency; and \( G' \) and \( G'' \) are the storage and loss moduli, respectively. Then, the component of the birefringence that is proportional to shear stress is

\[
n_{12} = \gamma_0 (B' \sin \omega t + B'' \cos \omega t) = (1/2)\Delta n' \sin(2\chi)
\]  

(5)

\( C \) is calculated as follows:

\[
C = \Delta n' \sin(2\chi)/(2\sigma_{12})
\]

RESULTS

Rheology

The viscoelastic moduli \( (G' \) and \( G'' \)) of L-PS and HBPS appear to obey time–temperature superposition over the temperature range used in this study [Fig. 3(a,b)]. To create a master curve, we used a reference temperature of 150 °C, with no vertical shift factors. The 13K-L-PS shows moduli characteristic of unentangled polymer behavior, as suggested by the absence of an entanglement plateau, whereas 171 K-L-PS develops a plateau modulus (\( G_N \)) estimated to be \( 1.56 \times 10^6 \text{ dyn/cm}^2 \) and an \( M_e \) value of 18,900 g/mol calculated from\(^{36} \)
where \( \rho \) is the density of molten polystyrene. The values obtained from our measurements agree with the literature value of 18,100 g/mol.31

Both 13K- and 171K-L-PS reach the terminal behavior, where \( G' \sim \omega^2 \) and \( G'' \sim \omega^1 \).37 In the high-frequency region, the dynamic moduli of all model polymers compare well with one another. However, differences between linear and branched polystyrenes are noticeable at low frequencies. \( G' \) of the weakly entangled 50K-R-HBPS shows an onset of a plateau, with an estimated \( G'_N \) of \( 2.1 \times 10^6 \) dyn/cm\(^2\) and an \( M_e \) of 14,100 g/mol. This value of \( G'_N \) is higher than that of 171K-L-PS. This is consistent with the observations of Hatzikiriakos et al.38 on polybutadiene stars; they found that a high degree of branching increased \( G'_N \) to a certain extent. 10K-R-HBPS does not show a plateau, even though its overall molecular weight is much higher than \( M_e \), suggesting that \( M_e \) is the critical factor in entanglement formation even in these systems, just as in symmetric stars.

The effect of architecture is even more evident in the terminal behavior. Although 50K-R-HBPS shows only a hint of nonterminal behavior (\( G' \sim \omega^{1.3} \), \( G'' \sim \omega^1 \)), 10K-R-HBPS shows even stronger deviation, with \( G' \sim \omega^{1.1} \) and \( G'' \sim \omega^{0.85} \). The horizontal shift factors (\( \alpha_T \)) of HBPS appear to show a different temperature dependence than those of L-PS, especially at high temperatures (Fig. 4). The temperature dependence of \( \alpha_T \) for HBPS is weaker than that of L-PS. Similar departures were observed by Graessley and coworkers7,39,40 for polybutadiene, polyisoprene, and poly(ethylene-alt-propylene) symmetric stars.

**Flow Birefringence**

Over the temperature and frequency range used in this study, both linear polymers obey the SOR [shown later in Fig. 5(a)]. A \( C \) value of \( -4.5 \times 10^{-10} \) cm\(^2\)/dyn describes the shear stress and corresponding component of the birefringence. This value agrees very well with the published literature value for L-PS.32,41 The magnitude of \( C \) of 13K-L-PS was found to be \( -3.5 \times 10^{-10} \) cm\(^2\)/dyn, which is somewhat lower than that of the high molecular weight polymer. For polystyrene melts, such strong molecular weight dependence was also observed by Kornfield and Verma,33 especially for a weight-average molecular weight (\( M_w \)) of less than 44,000 g/mol. The more complex relaxation process of low molecular weight polystyrenes was explained through the domination of nonentropic modes, extended to quite large length and time scales. Our preliminary studies showed that when a L-PS with a molecular weight of 19,000 g/mol was tested, \( C \) was \( -4.3 \times 10^{-10} \) cm\(^2\)/dyn. This is close to the value obtained for 171K-L-PS, suggesting that even though there is a molecular weight dependence of \( C \) of L-PS, it is significant only below a certain molecular weight. We address this issue in larger detail in a forthcoming article.21

To our knowledge, this is the first study on the melt flow birefringence behavior of HBPS melts. The HBPS used in this study showed a distinctly different stress-optical behavior compared with that of the linear polymers. The relatively high \( M_e \), 50K-R-HBPS appears to obey the SOR over a wide temperature range [Fig. 5(b)]. Both components of \( G^* \) calculated from the mechanical stress...
and optical birefringence are in a good agreement with each other.

The temperature dependence of $C$ as a function of molecular architecture is shown in Figure 6. In polystyrene, because the polarizability perpendicular to the chain is higher than that parallel to the chain, $C$ is negative. We plot the magnitude of $C$ for ease of comparison. $171K$-$L$-$PS$ shows a frequency-independent $C$ value of $-4.5 \times 10^{-10}$ cm$^2$/dyn, which is slightly temperature-dependent (as shown by the broadness of the data points), as expected. However, for $50K$-$R$-$HBPS$, $C = -3.7 \times 10^{-10}$ cm$^2$/dyn, which is lower than that of L-$PS$. The lower value was repeatable in different sample loadings.

However, $10K$-$R$-$HBPS$ demonstrates a clear breakdown in the SOR, even though it is a homopolymer melt [Fig. 6(b)]. Consistent with previous studies on SOR failures in miscible blends and copolymers, we plot both the magnitude of $C$ and the ratios of the real ($C' = B'/G'$) and imaginary parts ($C'' = B''/G''$) of the corresponding components of the shear stress and birefringence. At high frequencies, $C'$ and $C''$ are approximately equal, with an estimated value of $-1$. At intermediate frequencies, $C'$ and $C''$ are frequency-dependent, with the deviation in $C'$ appearing first at about 1 rad/s, followed by the deviation in $C''$ at about 0.01 rad/s. $C'$ is found to increase much more strongly than $C''$ as the frequency decreases. Such a breakdown of the SOR and the strong frequency dependence are very unusual for homopolymer melts.

**DISCUSSION**

Rheological and flow birefringence measurements on linear and controlled arm-length HBPS homopolymer melts reveal the unique role of branching architecture and branch length, especially when branch density is high.

The synthesis of these materials produces star-like HBPs, with the length of the arm fixed. As discussed in the Materials section, on the basis of the intrinsic viscosity and the small Mark–Houwink exponent, the HBPs appear to be spherical molecules. The branch density is especially high for $10K$-$R$-$HBPS$. In contrast to previous studies on highly entangled star polyisoprenes and polybutadienes, our materials are relatively unentangled. This allows for the rheology and flow birefringence to be affected more by the branching density than by the effects of entanglement.
The shift factors show slightly weaker temperature dependence at higher temperatures, compared with those of linear polymers. The weaker dependence may have been caused by differences in the fractional free volume and the expansion coefficient between linear and branched chain configurations. In addition, it is possible that there are additional contributions to the shear moduli due to the high density of branching that have a distinct temperature dependence compared with the segmental contributions.

Dynamic moduli of HBPS show nonterminal behavior, suggesting that, in addition to chain dynamics, there may be other relaxation mechanisms. Because the nonterminal behavior is manifested more in 10K-R-HBPS, such contributions may be more significant in this polymer. The exact nature of these modes is still under investigation, but more clues may be apparent from the stress-optical behavior.

In the region where the SOR holds, $C$ of HBP is significantly lower than that of linear polymers with the same $M_a$ or total molecular weight. Such a decrease in $C$ in these materials is more significant and qualitatively different from the molecular weight effect in L-PS. A complete breakdown in the SOR is observed in the 10K-R-HBPS sample. Quantitative measurements of such a breakdown can be an effective tool for studying contributions from different length scales in complex polymeric materials. For example, in lamellar diblock copolymers, nonuniform contributions to stress and birefringence from nanostructural orientation caused the SOR to fail. Analogous to the observations in a lamellar block copolymer, we observe a strong frequency dependence in $C$ ($C'$ and $C''$). At high frequencies, segmental contributions dominate birefringence and stress. At lower frequencies, contributions from larger length scales become important. For a lamellar diblock copolymer, it was the lamellar nanostructure. The stress-optical ratio showed a strong low-frequency response in that material. In 10K-R-HBPS, a homopolymer melt, the exact nature of such a length scale is not yet clear and is currently under investigation.

We hypothesize that the additional contributions may have origins in the branch density of these systems. It is possible that this leads to a preferential segmental orientation near the core of the branched polymer, as suggested by McLeish and Milner, similar to what is seen in soft-colloid materials. Such organization would produce a length scale that is larger than the segmental length. Evidence of this behavior in highly entangled, hyperstar polybutadienes was experimentally observed by Roovers and coworkers, using rheology, solution viscometry, and small-angle X-ray scattering. Apparently, the fact that our branched polymers are unentangled or weakly entangled may be allowing us to access this regime more easily. Because 10K-R-HBPS has a shorter arm and higher branch density, the SOR breaks down more strongly, further suggesting that the structural contributions to birefringence are more pronounced in this sample. Apparently, the orientation response of the core contributes much more strongly to birefringence than to stress at lower frequencies, thereby producing a higher stress-optical ratio. The elastic

Figure 6. Effect of the molecular architecture on (a) the magnitude of the stress-optical coefficient (SOC) and (b) the in-phase and out-of-phase components of the SOC for 10K-R-HBPS (reference temperature $= 150 ^\circ$C; different shades of the symbols represent data taken at different temperatures).
component of this contribution dominates the viscous component, as evidenced by the failure in $C'$ first.

If these highly branched homopolymer melts indeed show soft-colloid behavior, light scattering may be able to establish the length scale. It is to be expected that the size of the core would not be strongly dependent on $M_a$. Therefore, the breakdown of SOR should be more pronounced on a shorter arm polymer with the same number of arms. Currently, rheological, rheooptical, and light scattering studies are underway on controlled branch-length HBPSs of various $M_a$'s. As a comparison, symmetric stars are also being explored.

CONCLUSIONS

The rheological and rheooptical behavior of HBPS melts has been investigated over a wide dynamic range. The HBPS melts used in this study are relatively unentangled and have a large number of branches. Therefore, the unique role of branching was more easily manifested and was decoupled from entanglement dynamics. Quantitative comparisons of the rheology and flow birefringence of L-PS and HBPS melts provided glimpses of the polymeric and colloid-like nature in HBPS. Two L-PSs (molecular weights = 13,000 and 171,000 g/mol) and two starlike HBPSs (50K-R-HBPS, 15-arm, $M_a = 50,000$ g/mol, and 10K-R-HBPS, 50-arm, $M_a = 10,000$ g/mol) were investigated.

To our knowledge, this study represents the first measurements of stress-optical coefficients in HBPS melts. Our results suggest that

1. Both HBPS melts exhibited nonterminal behavior in rheology. Such behavior was more pronounced in 10K-R-HBPS.
2. 50K-R-HBPS obeyed the SOR but had a stress-optical coefficient of $-3.7 \times 10^{-10}$ cm$^2$/dyn, which was appreciably lower than that of a linear polymer of a corresponding $M_a$ or total molecular weight. This is a surprising result and suggests that highly branched polymers may have a lower intrinsic birefringence for a given amount of stress. This may be useful in applications, such as molding, for which lower substrate birefringence is desired.
3. 10K-R-HBPS showed a failure in the SOR, with a frequency-dependent stress-optical coefficient. The failure was apparent first in the in-phase component of $C$ and then in the out-of-phase component, thereby revealing the elastic nature of the additional contribution to birefringence.
4. The failure of the SOR in a polystyrene homopolymer melt is unusual. On the basis of the studies on the failure of the SOR in blends and block copolymers, we believe that this may occur from preferential orientation of chains near the core of the densely branched polymer. This may produce an intrinsic contribution to birefringence arising from the orientation of the core as a whole. Therefore, when branch density is high, HBPS may exhibit both polymeric and soft-colloid behavior. This hypothesis is consistent with the scattering measurements of Roovers and coworkers,\textsuperscript{18–20} who observed soft structures in highly entangled, 64-arm and 128-arm hyperstar polybutadienes. In our study, the lack of entanglements appears to make the manifestation of the structural contributions to birefringence easier. For an understanding of the exact nature and dynamics of the soft structures suggested by our results, complimentary techniques such as light scattering would be beneficial. Studies on L-PS, symmetric star polystyrene, and HBPS of various arm lengths are underway for the characterization of the length scale of the suggested soft cores and their effect on the rheology and orientation behavior.\textsuperscript{21} Light scattering, solution viscosity measurements, and rheooptical methods are being used for the systematic characterization of these materials.

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REFERENCES AND NOTES