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COMPLEX VISCOSITY OF STAR-BRANCHED MACROMOLECULES FROM ANALYTICAL GENERAL RIGID BEAD-ROD THEORY

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ABSTRACT

The complex viscosity of planar star-branched polymers has been derived from general rigid bead-rod theory, but only for singly-beaded arms. Here, we explore the respective roles of branch functionality, arm length and non-planar arrangements, analytically from general rigid bead-rod theory. For non-planar arrangements, we include polyhedral, both regular and irregular. Further, for all structures, we compare with and without the central bead. We fit the theory to complex viscosity measurements on polybutadiene solutions, one quadrafunctional star-branched, the other unbranched, of the same molecular weight ($M_w = 200,000$ g/gmol). We learn that when general rigid bead-rod theory is applied to quadrafunctional polybutadiene, a slightly irregular center-beaded tetrahedron of interior angle 134° is required (with 1,360,000 g/gmol per bead) to describe its complex viscosity behaviour.

Keywords: complex viscosity, general rigid bead-rod theory, star-branched polymers, planar, tetrahedron

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I. INTRODUCTION

The complex viscosity of planar star-branched polymers has been derived from general rigid bead-rod theory, but only for singly-beaded arms (Rows 3 and 4 of Table XV of [1] or Table 14 of [2]). Here, we explore the respective roles of branch functionality, arm length and non-planar arrangements analytically from general rigid bead-rod theory. For non-planar arrangements, we include polyhedral, both regular and irregular. Further, for all structures, we compare with and without the central bead. We test our new theory against the seminal complex viscosity measurements of [3,4] on polybutadiene solutions, branched *versus* unbranched.

We will compare our results with the well-known one for the zero-shear viscosity of unbranched chains (Row 1 of Table XV from [1] or Table 14 of [2]):

$$\frac{\eta_0^\ell}{n^\ell kT\lambda_0} = \frac{1}{6}N(N^2 - 1) \quad (1)$$

From Table 1 and Table XV of [1], Eq. (49) can be solved for unbranched chains ($N = N_A N_B + 1$):

$$\frac{\eta'}{nkT\lambda_0} = \frac{1}{15}N_A N_B (N_A N_B + 1)(N_A N_B + 2) \left\{ 1 + \frac{3}{2} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (2)$$

and:

$$\frac{\eta''}{nkT\lambda_0} = \frac{1}{15}N_A N_B (N_A N_B + 1)(N_A N_B + 2) \left\{ \frac{3}{2} \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (3)$$

As Eq. (2) $\lambda\omega \rightarrow 0$:

$$\frac{\eta_0^\ell}{nkT\lambda_0} = \frac{1}{6}N_A N_B (N_A N_B + 1)(N_A N_B + 2) \quad (4)$$

so that:

$$\frac{\eta'}{\eta_0^\ell} = \frac{2}{5} + \frac{3}{5} \left\{ \frac{1}{1 + (\lambda\omega)^2} \right\} \quad (5)$$

and:

$$\frac{\eta''}{\eta_0^\ell} = \frac{3}{5} \left\{ \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (6)$$

which we use to normalize our new results for star-branched polymers below. Figure 1 defines the unbranched chain.

We will also compare our results with the well-known one for the relaxation time of unbranched chains (Row 1 of Table XV from [1] or Table 14 of [2]):

$$\frac{\lambda^\ell}{\lambda_0} \equiv \frac{1}{6}N(N^2 - 1) \quad (7)$$

wherein:

$$N = N_A N_B + 1 \quad (8)$$

since we base our comparison on the seminal complex viscosity measurements of [3,4] on polybutadiene solutions, branched *versus* unbranched. We can introduce Eq. (8) because these measurements of [3,4] compare branched *versus* unbranched chains of the same molecular weight ($M_w = 200,000$ g/gmol). Thus:

$$\frac{\lambda^\ell}{\lambda_0} \equiv \frac{1}{6} N_A N_B (N_A N_B + 1)(N_A N_B + 2) \quad (9)$$

where $M = m_i N$, where m_i is the bead mass, which branching does not change.

II. METHOD

We locate each bead of mass m_i with the position vector of the i th bead $\mathbf{r}_i$, where the macromolecular center of mass $\mathbf{R}$ satisfies:

$$\sum_{i=1}^N m_i (\mathbf{r}_i - \mathbf{R}) = 0 \quad (10)$$

so that:

$$\mathbf{R} = \frac{1}{M} \sum_{i=1}^N m_i \mathbf{r}_i \quad (11)$$

where N is the total number of beads and $M \equiv \sum_{i=1}^N m_i$, the total mass. Since we construct our macromolecules, be they branched or not, with identical beads of diameter d and mass m , then $M \equiv mN$, and thus, the center of mass is:

$$\mathbf{R} = \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i \quad (12)$$

which we will use below.

We next install *molecular coordinates*, at the macromolecular center of mass, and we orient these Cartesian coordinates such that $\hat{\delta}_3$ is along the polar axis of the *moment of inertia ellipsoid* (MIE).

The position vector of the i th bead with respect to the center of mass given by (Eq. (16.7-16) of [5] or Eq. (13.6-16) of [6]):

$$\mathbf{R}_i \equiv [R_{i1}, R_{i2}, R_{i3}] \quad (13)$$

We can define the principal moments of inertia I_1 , I_2 , and I_3 by (Eqs. (16.7-17) and (16.7-18) of [5], or (13.6-17) and (13.6-18) of [6]):

$$I_1 = m \sum_{i=1}^N (R_{i2}^2 + R_{i3}^2) \quad (14)$$

$$I_2 = m \sum_{i=1}^N (R_{i1}^2 + R_{i3}^2) \quad (15)$$

$$I_3 = 2m \sum_{i=1}^N R_{i1}^2 \quad (16)$$

where the subscript i is the bead number.

When the macromolecule is oblate:

$$I_3 > I_1 \quad (17)$$

and for prolate:

$$I_3 < I_1 \quad (18)$$

Our general rigid bead-rod theory just applies to axisymmetric macromolecules. By *axisymmetric*, we mean:

$$I_1 = I_2 \quad (19)$$

For general rigid bead-rod theory, Hassager derives the expression for the shear relaxation function:

$$G(s) \equiv (2\eta_s + n\xi L^2 a)\delta(s) + nkTbe^{-s/\lambda} \quad (20)$$

in which (Eqs. (16.7-38) of [7] or Eqs. (13.6-44), (13.6-45), and (13.6-46) of [8]):

$$a \equiv \frac{2I_1 + I_3}{6mL^2} - \frac{(I_1 - I_3)^2}{5I_1 mL^2} \quad (21)$$

$$b \equiv \frac{3(I_1 - I_3)^2}{5I_1^2} \quad (22)$$

$$\nu \equiv \frac{6mL^2}{I_1} \quad (23)$$

where (first paragraph of Section VI.b, above Eq. (44) of [9]):

$$0 \leq b \leq \frac{3}{5} \quad (24)$$

The three quantities a , b and ν thus define completely the differences in linear viscoelastic behaviors arising between different axisymmetric macromolecular structures. Whereas we associate a with the Dirac delta function contribution to the relaxation function, we associate b with the dying exponential. From **FIG. 3** of [1], we learn that:

$$\frac{4}{5} < a\nu < \frac{77}{24} \quad (25)$$

and since $\nu > 0$ [see its definition, Eq. (23)], $a > 0$. Combining this with Eq. (21) yields, for all axisymmetric macromolecules:

$$\frac{(I_1 - I_3)^2}{I_1(2I_1 + I_3)} < \frac{5}{6} \quad (26)$$

which is new.

The macromolecular relaxation time can be expressed as:

$$\lambda \equiv \frac{\xi I_1}{6mkT} \equiv \frac{\xi L^2}{\nu kT} \quad (27)$$

where the bead friction coefficient is:

$$\xi \equiv 3\pi d\eta_s \quad (28)$$

and, for the rigid dumbbell (Eq. (6) of [10]):

$$\lambda_0 \equiv \frac{\xi L^2}{12kT} \equiv \frac{\pi d\eta_s L^2}{4kT} \quad (29)$$

and where Figure 1 through Figure 5 define center-to-center distances between nearest neighbors, L .

Macromolecular lopsidedness, $2b/av$, is the extent to which the branched macromolecule deviates from a spherically symmetrical structure:

$$0 \leq \frac{2b}{av} \leq \frac{3}{2} \quad (30)$$

The minimum value of 0 is for spherically symmetrical branched structures such as the symmetric rigid octahedron, and the maximum value is 3/2 for long slender bodies such as the rigid dumbbell or the multi bead-rod, also known as “shish-kebab” [1]. Dividing Eqs. (27) by Eq. (29) normalizes the relaxation time of the general macromolecule to that of the simplest:

$$\frac{\lambda}{\lambda_0} \equiv \frac{12}{\nu} \quad (31)$$

We can then use Eq. (20) to calculate the polymer contribution to the stress tensor in any linear viscoelastic flow, including oscillatory shear flow, from (Eq. (1) of [11]).

$$\boldsymbol{\tau}_p \equiv - \int_{-\infty}^t G(t-t') \dot{\boldsymbol{\gamma}}(t') dt' \quad (32)$$

where all symbols are defined in Table 2 and Table 3.

a. OSCILLATORY SHEAR FLOW

We measure the complex viscosity in oscillatory shear flow, generated by confining the fluid to a simple shear apparatus and then by subjecting one solid-liquid boundary to a coplanar sinusoidal displacement generating the corresponding cosinusoidal shear rate:

$$\dot{\gamma}(t) = \dot{\gamma}^0 \cos \omega t \quad (33)$$

such that, the rate of deformation tensor is given by:

$$\dot{\boldsymbol{\gamma}}(t) = \begin{bmatrix} 0 & \dot{\gamma}^0 \cos \omega t & 0 \\ \dot{\gamma}^0 \cos \omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (34)$$

Using the characteristic relaxation time of the branched polymeric viscoelastic fluid, λ , we can nondimensionalize Eq. (33) as:

$$\lambda \dot{\gamma}(t) = \lambda \dot{\gamma}^0 \cos \lambda \omega (t/\lambda) \quad (35)$$

where, $\lambda \omega$ and $\lambda \dot{\gamma}^0$ are the Deborah and Weissenberg numbers. In this paper, we focus on small-amplitude oscillatory shear flow (SAOS). For this flow field, for the molecular definition of *small amplitude*, general rigid bead-rod theory yields:

$$\lambda \dot{\gamma}^0 \ll \frac{1}{\nu \sqrt{2}} \quad (36)$$

whose left side is the macromolecular Weissenberg number. From Eq. (36), we learn that branched structures with higher ν will have lower limits for linear viscoelasticity.

To oscillatory shear flow, polymeric liquids respond with shear stress, and also with normal stress differences. When Eq. (36) is satisfied, the shear stress response is sinusoidal:

$$\tau_{21} = -\dot{\gamma}^0 (\eta'(\omega) \cos \omega t + \eta''(\omega) \sin \omega t) \quad (37)$$

with parts in-phase and out-of-phase with the shear rate [12]. We follow the Gemant convention [13,14,15]:

$$\eta^* \equiv \eta' - i\eta'' \quad (38)$$

Substituting Eq. (31) of [1] and [16], for general rigid bead-rod theory, for the polymer contribution to the real part of the complex viscosity we get:

$$\frac{(\eta' - \eta_s)}{nkT\lambda_0} = 6a \left\{ 1 + \frac{2b}{av} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (39)$$

and for *minus* the imaginary part (Eq. (34) of [1]):

$$\frac{\eta''}{nkT\lambda_0} = 6a \left\{ \frac{2b}{av} \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (40)$$

from which we learn that $b > 0$ is necessary for the fluid to exhibit elasticity in oscillatory shear flow. In other words, the dying exponential term in Eq. (20) is the source of the fluid elasticity. From Eqs. (39) and (40) both η' and η'' are amplified by the same factor $1/nkT\lambda_0$.

Eqs. (39) and (40) are subject to inequalities Eq. (24) for b , and (below **TABLE 16.7-1** of [5]) and Eq. (30) for the macromolecular lopsidedness. As $\lambda\omega \rightarrow 0$, Eqs. (39) and (40) give:

$$\frac{(\eta_0 - \eta_s)}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow 0} \frac{(\eta' - \eta_s)}{nkT\lambda_0} = 6a \left\{ 1 + \frac{2b}{av} \right\} \quad (41)$$

$$\frac{\eta''_0}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow 0} \frac{\eta''}{nkT\lambda_0} = 0 \quad (42)$$

and, as $\lambda\omega \rightarrow \infty$:

$$\frac{(\eta'_\infty - \eta_s)}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow \infty} \frac{(\eta' - \eta_s)}{nkT\lambda_0} = 6a \quad (43)$$

$$\frac{\eta''_\infty}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow \infty} \frac{\eta''}{nkT\lambda_0} = 0 \quad (44)$$

where limits, Eqs. (41) and (43), are subject to Eqs. (24) and (30).

Nondimensionalizing Eqs. (39) and (40) with Eq. (41) yields:

$$\frac{\eta' - \eta_s}{\eta_0 - \eta_s} = \left\{ 1 + \frac{2b}{av} \right\}^{-1} \left\{ 1 + \frac{2b}{av} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (45)$$

and:

$$\frac{\eta''}{\eta_0 - \eta_s} = \left\{ 1 + \frac{2b}{av} \right\}^{-1} \left\{ \frac{2b}{av} \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (46)$$

which are universal results from general rigid bead-rod theory, applying to any suspension of axisymmetric macromolecules. In this work, we will derive special cases of Eqs. (45) and (46) for suspensions of star-branched polymers, be they center-beaded or center-ringed.

Solving Eq. (39) for the real part of the complex viscosity, we get:

$$\frac{\eta'}{nkT\lambda_0} = 6a \left\{ 1 + \frac{2b}{av} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} + \frac{\eta_s}{nkT\lambda_0} \quad (47)$$

and if:

$$\frac{\eta_s}{nkT\lambda_0} \ll 1 \quad (48)$$

then solvent viscosity does not matter. Since the left side of Eq. (48) does not contain macromolecular constants, that is, neither a , nor b , nor v , we see that the negligibility of

solvent viscosity does not depend on the branching structure. When Eq. (48) obtains, we get:

$$\frac{\eta'}{nkT\lambda_0} = 6a \left\{ 1 + \frac{2b}{av} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (49)$$

which we will use presently.

III. RESULTS: PLANAR STARS

For equidimensional branching, the total number of beads in a center-beaded planar star is given by Eq. (8), and in a center-ringed one:

$$N = N_A N_B \quad (50)$$

where N_A is the total number of arms on the macromolecule, N_B , the number of beads on an arm (excluding the center bead), and the product $N_A N_B$ is thus always a multiple of N_A .

For $3 \leq N_A \leq 6$, we position our Cartesian molecular z -axis normal to and centered on the planar star. The position vector with respect to the center of mass for each bead of a planar star on the n th arm is given by (Eqs. (16.7-17) of [6] or Eqs. (13.6-17) of [17]):

$$\mathbf{R}_{n,c} = [cL \cos \theta_n, cL \sin \theta_n, 0] \quad (51)$$

where the first arm, $n = 1$, is along our molecular x -axis, with arms following counter-clockwise enumeration, and c is the bead number along each branch, counted radially from the center ($c = 0$). Figure 2 and Figure 3 illustrate these definitions. The branch angle, measured counter-clockwise in the plane of the star, and from our molecular x -axis, is given by:

$$\theta_n = (n - 1) \frac{2\pi}{N_A} \quad (52)$$

which is subject to:

$$1 \leq n \leq N_A \quad (53)$$

which will use presently. In the following subsections, we examine center-beaded planar stars and their center-ringed counterparts. Since all planar stars are oblate, Eq. (17) applies to both of the following subsections. Otherwise put, $N_B > 2$.

For $N_A \geq 7$, we position our Cartesian molecular z -axis normal to and centered on the planar star. The position vector with respect to the center of mass for each bead of a planar star on the n th arm is given by (Eqs. (16.7-17) of [6] or Eqs. (13.6-17) of [17]):

$$\mathbf{R}_{n,c} = \left[cL \frac{\cos \theta_n}{2 \sin \left(\frac{\pi}{N_A} \right)}, cL \frac{\sin \theta_n}{2 \sin \left(\frac{\pi}{N_A} \right)}, 0 \right] \quad (54)$$

where the first arm, $n = 1$, is along our molecular x -axis, with arms following counter-clockwise enumeration, and c is the bead number along each branch, counted radially from the center ($c = 0$). Figure 4 and Figure 5 illustrate these definitions.

a. CENTER-BEADED PLANAR STARS ($3 \leq N_A \leq 6$)

For center-beaded planar stars, Eqs. (51) and (52) are subject to Eqs. (53) and:

$$1 \leq c \leq N_B \quad (55)$$

Substituting Eq. (51) into Eqs. (14) through (16), we get the principal moments of inertia for a center-beaded planar star:

$$I_1 \equiv mL^2 \sum_{c=1}^{c=N_B} c^2 \sum_{n=1}^{n=N_A} \sin^2 \theta_n \equiv mL^2 Z \alpha \quad (56)$$

$$I_2 \equiv mL^2 \sum_{c=1}^{c=N_B} c^2 \sum_{n=1}^{n=N_A} \cos^2 \theta_n \equiv mL^2 Z \beta \quad (57)$$

$$I_3 \equiv 2mL^2 \sum_{c=1}^{c=N_B} c^2 \sum_{n=1}^{n=N_A} \cos^2 \theta_n \equiv 2mL^2 Z \beta \quad (58)$$

From Eq. (52), and Eqs. (56) through (58), we get:

$$Z \equiv \sum_{c=1}^{c=N_B} c^2 = N_B(N_B + 1)(2N_B + 1) \quad (59)$$

$$\alpha \equiv \sum_{n=1}^{n=N_A} \sin^2 \theta_n = \sum_{n=1}^{n=N_A} \sin^2 \left[(n-1) \frac{2\pi}{N_A} \right] = \frac{N_A}{2} \quad (60)$$

$$\beta \equiv \sum_{n=1}^{n=N_A} \cos^2 \theta_n = \sum_{n=1}^{n=N_A} \cos^2 \left[(n-1) \frac{2\pi}{N_A} \right] = \frac{N_A}{2} = \alpha \quad (61)$$

Substituting Eqs. (59) and (60) into Eq. (56) gives:

$$I_1 \equiv \frac{N_A}{2} N_B(N_B + 1)(2N_B + 1)mL^2 \quad (62)$$

and Eqs. (59) and (61) into Eq. (57):

$$I_2 \equiv \frac{N_A}{2} N_B(N_B + 1)(2N_B + 1)mL^2 = I_1 \quad (63)$$

and Eqs. (59) and (61) into Eq. (58):

$$I_3 \equiv N_A N_B(N_B + 1)(2N_B + 1)mL^2 \quad (64)$$

Substituting Eqs. (62) through (64) into Eqs. (21) through (23) gives the orientation constants for a center-beaded planar star branched polymer:

$$a \equiv \frac{7}{30} N_A N_B(N_B + 1)(2N_B + 1) \quad (65)$$

$$b \equiv \frac{3}{5} \quad (66)$$

$$v \equiv \frac{12}{N_A N_B(N_B + 1)(2N_B + 1)} \quad (67)$$

Multiplying a by v gives:

$$av = \frac{14}{5} \quad (68)$$

as it must, for $b = 3/5$ (see FIG 3 of [1]). Inserting Eq. (67) into Eq. (31) yields:

$$\frac{\lambda}{\lambda_0} \equiv N_A N_B(N_B + 1)(2N_B + 1) \quad (69)$$

for center-beaded stars with $3 \leq N_A \leq 6$.

Eqs. (65) through (67) are subject to Eq. (26). Substituting Eqs. (66) and (68) into Eqs. (45) and (46) yields, for suspensions of center-beaded planar star-branched polymers:

$$\frac{\eta' - \eta_s}{\eta_0 - \eta_s} = \frac{7}{10} \left\{ 1 + \frac{3}{7} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (70)$$

and:

$$\frac{\eta''}{\eta_0 - \eta_s} = \frac{3}{10} \left\{ \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (71)$$

which we will recover, from time to time, below. Eqs. (70) and (71) are special cases of Eqs. (45) and (46).

Substituting Eqs. (62) and (64) into Eq. (26) gives, for all center-beaded planar stars:

$$\frac{1}{4} < \frac{5}{6} \quad (72)$$

as it should.

The uninitiated might expect the special case of the N -bead shish-kebab, namely, the 2-arm center-beaded star with $\frac{1}{2}(N - 1)$ beads on each arm [$N_A = 2, N_B = \frac{1}{2}(N - 1)$] to be relevant here. However, whereas all planar stars are oblate, all shish-kebabs are prolate.

For Eqs. (65) and (67), we next examine their special cases of the N -bead star-branched polymer, with single-beaded arms ($N_A = N - 1, N_B = 1$):

$$a \equiv \frac{7}{30} (N - 1) \quad (73)$$

and:

$$v \equiv \frac{12}{N - 1} \quad (74)$$

which match row 3 of Table 1 (or row 3 of Table XV of [1]), as they must.

Substituting Eqs. (65) through (67) into Eqs. (49) and (40):

$$\frac{\eta'}{nkT\lambda_0} = \left[\frac{7}{5} (N_A N_B (N_B + 1) (2N_B + 1)) \right] \left\{ 1 + \frac{3}{7} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (75)$$

$$\frac{\eta''}{nkT\lambda_0} = \left[\frac{7}{5} (N_A N_B (N_B + 1) (2N_B + 1)) \right] \left\{ \frac{3}{7} \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (76)$$

as $\lambda\omega \rightarrow 0$:

$$\frac{\eta_0}{nkT\lambda_0} = 2N_A N_B (N_B + 1) (2N_B + 1) \quad (77)$$

so that:

$$\frac{\eta'}{\eta_0} = \frac{7}{10} \left\{ 1 + \frac{3}{7} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (78)$$

and:

$$\frac{\eta''}{\eta_0} = \frac{3}{10} \left\{ \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (79)$$

illustrated in Figure 6 and Figure 7, which expand as:

$$\frac{\eta'}{\eta_0} = 1 - \frac{3}{10} [(\lambda\omega)^2 - (\lambda\omega)^4 + \dots] \quad (80)$$

and:

$$\frac{\eta''}{\eta_0} = \frac{3}{10} [\lambda\omega - (\lambda\omega)^3 + \dots] \quad (81)$$

From the $(\lambda\omega)^2$ and $\lambda\omega$ terms of Eqs. (80) and (81) respectively, we learn about how (and how quickly) our center-beaded star suspension departs from its Newtonian equilibrium behaviour. Eqs. (78) and (79) are special cases of Eqs. (70) and (71), where $\eta_0 \gg \eta_s$. From Eqs. (78) and (79) we learn that for all planar center-beaded star suspensions, from general rigid bead-rod theory, both the real and imaginary parts of the complex viscosity share the same shapes for their frequency dependencies. Otherwise put, differences between star architectures shall just manifest in their λ and η_0 (following Eqs. (69) and (77) for $3 \leq N_A \leq 6$).

To deepen our understanding of how branching affects the rheology of center-beaded planar stars ($3 \leq N_A \leq 6$), we can normalize our main result, Eq. (77), with Eq. (4):

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{12(N_B + 1)(2N_B + 1)}{(N_A N_B + 1)(N_A N_B + 2)} \quad (82)$$

and Eq. (69), with Eq. (9):

$$\frac{\lambda}{\lambda^\ell} = \frac{6(N_B + 1)(2N_B + 1)}{(N_A N_B + 1)(N_A N_B + 2)} \quad (83)$$

where the superscripted ℓ indicates unbranched.

b. CENTER-RINGED PLANAR STARS ($3 \leq N_A \leq 6$)

For center-ringed planar stars, Eqs. (51) and (52) are subject to Eqs. (53) and:

$$2 \leq c \leq N_B \quad (84)$$

Substituting Eq. (51) into Eqs. (14) through (16), we get the principal moments of inertia for a center-ringed planar star:

$$I_1 \equiv mL^2 \left(-1 + \sum_{c=1}^{c=N_B} c^2 \right) \sum_{n=1}^{n=N_A} \sin^2 \left[(n-1) \frac{2\pi}{N_A} \right] \equiv mL^2 (-1 + Z) \alpha \quad (85)$$

$$I_2 \equiv mL^2 \left(-1 + \sum_{c=1}^{c=N_B} c^2 \right) \sum_{n=1}^{n=N_A} \cos^2 \left[(n-1) \frac{2\pi}{N_A} \right] \equiv mL^2 (-1 + Z) \beta \quad (86)$$

$$I_3 \equiv 2mL^2 \left(-1 + \sum_{c=1}^{c=N_B} c^2 \right) \sum_{n=1}^{n=N_A} \cos^2 \left[(n-1) \frac{2\pi}{N_A} \right] \equiv 2mL^2 (-1 + Z) \beta \quad (87)$$

Substituting Eqs. (59) through (61) into Eqs. (85) through (87) gives:

$$I_1 \equiv mL^2 [-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{2} \quad (88)$$

$$I_2 \equiv mL^2 [-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{2} = I_1 \quad (89)$$

$$I_3 \equiv mL^2 [-1 + N_B(N_B + 1)(2N_B + 1)] N_A \quad (90)$$

Substituting Eqs. (88) through (90) into Eqs. (21) through (23) gives the orientation constants for a center-ringed planar star branched polymer:

$$a \equiv \frac{7}{30} [-1 + N_B(N_B + 1)(2N_B + 1)]N_A \quad (91)$$

$$b \equiv \frac{3}{5} \quad (92)$$

$$v \equiv \frac{12}{[-1 + N_B(N_B + 1)(2N_B + 1)]N_A} \quad (93)$$

Multiplying a by v gives:

$$av = \frac{14}{5} \quad (94)$$

as it must, for $b = 3/5$ (see FIG 3 of [1]). Inserting Eq. (93) into Eq. (31) yields:

$$\frac{\lambda}{\lambda_0} \equiv N_A [-1 + N_B(N_B + 1)(2N_B + 1)] \quad (95)$$

for center-ringed stars with $3 \leq N_A \leq 6$.

Eqs. (91) through (93) are subject to Eq. (26). Substituting Eqs. (88) and (90) into Eq. (26) gives, for all center-ringed planar stars:

$$\frac{1}{4} < \frac{5}{6} \quad (96)$$

as it should.

We next examine the special case of the N -bead star-branched polymer, with single-beaded arms ($N_A = N, N_B = 1$):

$$a \equiv \frac{7}{6} N \quad (97)$$

and:

$$v \equiv \frac{12}{5N} \quad (98)$$

which match row 3 of Table 1 (or row 3 of Table XV of [1]), as they must.

Substituting Eqs. (91) through (93) into Eqs. (49) and (40):

$$\frac{\eta'}{nkT\lambda_0} = \frac{7}{5} [-1 + N_B(N_B + 1)(2N_B + 1)]N_A \left\{ 1 + \frac{3}{7} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (99)$$

$$\frac{\eta''}{nkT\lambda_0} = \frac{3}{5} [-1 + N_B(N_B + 1)(2N_B + 1)]N_A \left\{ \frac{1}{1 + (\lambda\omega)^2} \right\} \quad (100)$$

as $\lambda\omega \rightarrow 0$:

$$\frac{\eta_0}{nkT\lambda_0} = 2[-1 + N_B(N_B + 1)(2N_B + 1)]N_A \quad (101)$$

resulting in the same equations for η'/η_0 and η''/η_0 for center-ringed when $N_A \leq 6$ as center-beaded when $3 \leq N_A \leq 6$ [Eqs. (80) and (81)], illustrated in Figure 6 and Figure 7.

To deepen our understanding of how branching affects the rheology of center-ringed planar stars ($3 \leq N_A \leq 6$), we can normalize our main result, Eq. (101), with Eq. (4):

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{12(N_B + 1)(2N_B + 1)}{(N_A N_B + 1)(N_A N_B + 2)} - \frac{12}{N_B(N_A N_B + 1)(N_A N_B + 2)} \quad (102)$$

and Eq. (69), with Eq. (9):

$$\frac{\lambda}{\lambda^\ell} = \frac{6(N_B + 1)(2N_B + 1)}{(N_A N_B + 1)(N_A N_B + 2)} - \frac{6}{N_B(N_A N_B + 1)(N_A N_B + 2)} \quad (103)$$

where the superscripted ℓ indicates unbranched.

c. CENTER-BEADED PLANAR STARS ($N_A \geq 7$)

For center-beaded planar stars, Eqs. (54) and (52) are subject to Eqs. (53) and:

$$1 \leq c \leq N_B \quad (104)$$

Substituting Eq. (54) into Eqs. (14) through (16), we get the principal moments of inertia for a center-beaded planar star:

$$I_1 \equiv m L^2 \sum_{c=1}^{c=N_B} c^2 \sum_{n=1}^{n=N_A} \frac{\sin^2 \left[(n-1) \frac{2\pi}{N_A} \right]}{4 \sin^2 \left(\frac{\pi}{N_A} \right)} \equiv m L^2 Z \alpha_c \quad (105)$$

$$I_2 \equiv m L^2 \sum_{c=1}^{c=N_B} c^2 \sum_{n=1}^{n=N_A} \frac{\cos^2 \left[(n-1) \frac{2\pi}{N_A} \right]}{4 \sin^2 \left(\frac{\pi}{N_A} \right)} \equiv m L^2 Z \beta_c \quad (106)$$

$$I_3 \equiv 2 m L^2 \sum_{c=1}^{c=N_B} c^2 \sum_{n=1}^{n=N_A} \frac{\cos^2 \left[(n-1) \frac{2\pi}{N_A} \right]}{4 \sin^2 \left(\frac{\pi}{N_A} \right)} \equiv 2 m L^2 Z \beta_c \quad (107)$$

From Eq. (59) and Eqs. (105) through (107), we get:

$$\alpha_c \equiv \sum_{n=1}^{n=N_A} \frac{\sin^2 \theta_n}{4 \sin^2 \frac{\pi}{N_A}} = \sum_{n=1}^{n=N_A} \sin^2 \left[(n-1) \frac{2\pi}{N_A} \right] \sum_{n=1}^{n=N_A} \frac{1}{4 \sin^2 \frac{\pi}{N_A}} = \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}} \quad (108)$$

$$\beta_c \equiv \sum_{n=1}^{n=N_A} \frac{\cos^2 \theta_n}{4 \sin^2 \frac{\pi}{N_A}} = \sum_{n=1}^{n=N_A} \cos^2 \left[(n-1) \frac{2\pi}{N_A} \right] \sum_{n=1}^{n=N_A} \frac{1}{4 \sin^2 \left(\frac{\pi}{N_A} \right)} = \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}} \quad (109)$$

$$= \alpha_c$$

Substituting Eqs. (59) and (108) into Eq. (105) gives:

$$I_1 \equiv \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}} N_B (N_B + 1) (2N_B + 1) m L^2 \quad (110)$$

and Eqs. (59) and (109) into Eq.(106):

$$I_2 \equiv \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}} N_B (N_B + 1) (2N_B + 1) m L^2 = I_1 \quad (111)$$

and Eqs. (59) and (109) into Eq. (107):

$$I_3 \equiv \frac{N_A}{4 \sin^2 \frac{\pi}{N_A}} N_B (N_B + 1) (2N_B + 1) m L^2 \quad (112)$$

Substituting Eqs.(110) through (112) into Eqs. (21) through (23) gives the orientation constants for a center-beaded planar star branched polymer:

$$a \equiv \frac{7}{120 \sin^2 \frac{\pi}{N_A}} N_A N_B (N_B + 1) (2N_B + 1) \quad (113)$$

$$b \equiv \frac{3}{5} \quad (114)$$

$$v \equiv \frac{48 \sin^2 \frac{\pi}{N_A}}{N_A N_B (N_B + 1) (2N_B + 1)} \quad (115)$$

which match Row 4 of Table 1 (or Row 4 of Table XV of [1]), as they must.

Multiplying a by v gives:

$$av = \frac{14}{5} \quad (116)$$

as it must, for $b = 3/5$ (see FIG 3 of [1]). Inserting Eq. (115) into Eq. (31) yields:

$$\frac{\lambda}{\lambda_0} \equiv \frac{N_A N_B (N_B + 1) (2N_B + 1)}{4 \sin^2 \frac{\pi}{N_A}} \quad (117)$$

for center-beaded stars with $N_A \geq 7$.

Eqs. (113) through (115) are subject to Eq. (26). Substituting Eqs.(110) and (112) into Eq. (26) gives, for all center-beaded planar stars:

$$\frac{1}{4} < \frac{5}{6} \quad (118)$$

as it should.

Substituting Eqs. (113) through (115) into Eqs. (49) and (40):

$$\frac{\eta'}{nkT\lambda_0} = \frac{7}{20 \sin^2 \frac{\pi}{N_A}} N_A N_B (N_B + 1) (2N_B + 1) \left\{ 1 + \frac{3}{7} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (119)$$

$$\frac{\eta''}{nkT\lambda_0} = \frac{3}{20 \sin^2 \frac{\pi}{N_A}} N_A N_B (N_B + 1) (2N_B + 1) \left\{ \frac{1}{1 + (\lambda\omega)^2} \right\} \quad (120)$$

as $\lambda\omega \rightarrow 0$:

$$\frac{\eta_0}{nkT\lambda_0} = \frac{1}{2 \sin^2 \frac{\pi}{N_A}} N_A N_B (N_B + 1) (2N_B + 1) \quad (121)$$

resulting in the same equations for η'/η_0 and η''/η_0 for center-beaded when $N_A \geq 7$ as center-beaded when $3 \leq N_A \leq 6$ [Eqs. (80) and (81)], illustrated in Figure 6 and Figure 7.

d. CENTER-RINGED PLANAR STARS ($N_A \geq 7$)

For center-ringed planar stars, Eqs. (51) and (52) are subject to Eqs. (53) and (84). Substituting Eq. (51) into Eqs. (14) through (16), we get the principal moments of inertia for a center-ringed planar star:

$$I_1 \equiv mL^2 \left(-1 + \sum_{c=1}^{c=N_B} c^2 \right) \sum_{n=1}^{n=N_A} \frac{\sin^2 \left[(n-1) \frac{2\pi}{N_A} \right]}{4 \sin^2 \frac{\pi}{N_A}} \equiv mL^2 (-1 + Z) \alpha_c \quad (122)$$

$$I_2 \equiv mL^2 \left(-1 + \sum_{c=1}^{c=N_B} c^2 \right) \sum_{n=1}^{n=N_A} \frac{\cos^2 \left[(n-1) \frac{2\pi}{N_A} \right]}{4 \sin^2 \frac{\pi}{N_A}} \equiv mL^2 (-1 + Z) \beta_c \quad (123)$$

$$I_3 \equiv 2mL^2 \left[\left(-1 + \sum_{c=1}^{c=N_B} c^2 \right) \sum_{n=1}^{n=N_A} \frac{\cos^2 \left((n-1) \frac{2\pi}{N_A} \right)}{4 \sin^2 \frac{\pi}{N_A}} \right] \equiv 2mL^2 (-1 + Z) \beta_c \quad (124)$$

Substituting Eqs. (59), (108), and (109) into Eqs. (122) through (124) gives:

$$I_1 \equiv mL^2 [-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}} \quad (125)$$

$$I_2 \equiv mL^2 [-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}} = I_1 \quad (126)$$

$$I_3 \equiv mL^2 [-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{4 \sin^2 \frac{\pi}{N_A}} \quad (127)$$

Substituting Eqs. (125) through (127) into Eqs. (21) through (23) gives the orientation constants for a center-ringed planar star branched polymer:

$$a \equiv \frac{7}{120 \sin^2 \frac{\pi}{N_A}} [-1 + N_B(N_B + 1)(2N_B + 1)] N_A \quad (128)$$

$$b \equiv \frac{3}{5} \quad (129)$$

$$v \equiv \frac{48 \sin^2 \frac{\pi}{N_A}}{(-1 + N_B(N_B + 1)(2N_B + 1)) N_A} \quad (130)$$

as it must, for $b = 3/5$ (see FIG 3 of [1]), which match row 4 of Table 1 (or row 4 of Table XV of [1]), as they must. Inserting Eq. (130) into Eq. (31) yields:

$$\frac{\lambda}{\lambda_0} \equiv \frac{[-1 + N_B(N_B + 1)(2N_B + 1)] N_A}{4 \sin^2 \frac{\pi}{N_A}} \quad (131)$$

for center-beaded stars with $N_A > 7$.

Eqs. (128) through (130) are subject to Eq. (26). Substituting Eqs. (128) through (130) into Eq. (26) gives, for all center-ringed planar stars:

$$\frac{1}{4} < \frac{5}{6} \quad (132)$$

as it should.

Substituting Eqs. (128) through (130) into Eqs. (49) and (40):

$$\frac{\eta'}{nkT\lambda_0} = \frac{7}{20 \sin^2 \frac{\pi}{N_A}} [-1 + N_B(N_B + 1)(2N_B + 1)]N_A \left\{ 1 + \frac{3}{7} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (133)$$

$$\frac{\eta''}{nkT\lambda_0} = \frac{3}{20 \sin^2 \frac{\pi}{N_A}} [-1 + N_B(N_B + 1)(2N_B + 1)]N_A \left\{ \frac{1}{1 + (\lambda\omega)^2} \right\} \quad (134)$$

as $\lambda\omega \rightarrow 0$:

$$\frac{\eta_0}{nkT\lambda_0} = \frac{1}{2 \sin^2 \frac{\pi}{N_A}} [-1 + N_B(N_B + 1)(2N_B + 1)]N_A \quad (135)$$

resulting in the same equations for η'/η_0 and η''/η_0 for center-ringed when $N_A \geq 7$ as center-beaded when $3 \leq N_A \leq 6$ [Eqs. (80) and (81)], illustrated in Figure 6 and Figure 7.

IV. RESULTS: TETRAHEDRAL STARS

In spherical coordinates, the bead positions for the irregular tetrahedra between osculated and planar are:

$$\phi = 0, \pi, \frac{\pi}{2}, \frac{3\pi}{2} \quad (136)$$

$$\theta = \theta_1, \theta_1, \pi - \theta_1, \pi - \theta_1 \quad (137)$$

where:

$$\sin^{-1} \frac{d}{2L} \leq \theta_1 \leq \frac{\pi}{2} \quad (138)$$

or:

$$\sin^{-1} \frac{d}{2L} \leq \theta_1 \leq 90^\circ \quad (139)$$

where $\theta_1 = \frac{\pi}{2}$ is the planar 4-arm star, and where $\frac{1}{2}(\pi - \theta_t) = 0.62$ rad corresponds to the regular tetrahedron (spherically symmetric). By *osculated* we mean that θ_1 is such that the first beads on adjacent branches kiss. Here, $\theta_t \equiv \cos^{-1}(-\frac{1}{3}) \cong \frac{\pi}{2} + \frac{2\sqrt{2}}{9} \cong 109.5^\circ$ and is the *tetrahedral angle* of organic chemistry.

a. CENTER-BEADED TETRAHEDRAL STARS ($N_A = 4$)

On the unit sphere:

$$\mathbf{R}_i = \begin{cases} (0, \theta, \phi) \\ (1, \theta_1, 0) \\ (1, \theta_1, \pi) \\ \left(1, \pi - \theta_1, \frac{\pi}{2}\right) \\ \left(1, \pi - \theta_1, \frac{3\pi}{2}\right) \end{cases} \quad (140)$$

defined by Figure 8, where, in Cartesian coordinates (Eqs. (A.6-19) through (A.6-21) of [18]):

$$R_{i1} = \sin\theta\cos\phi \quad (141)$$

$$R_{i2} = \sin\theta\sin\phi \quad (142)$$

$$R_{i3} = \cos\theta \quad (143)$$

which are subject to Eqs. (136) and (137), so that:

$$\mathbf{R}_i = cL \begin{cases} (0,0,0) \\ (\sin\theta_1, 0, \cos\theta_1) \\ (-\sin\theta_1, 0, \cos\theta_1) \\ (0, \sin(\pi - \theta_1), \cos(\pi - \theta_1)) \\ (0, -\sin(\pi - \theta_1), \cos(\pi - \theta_1)) \end{cases} \quad (144)$$

which is subject to Eq. (138), and where $c = 1, 2, \dots, N_B$. Figure 9 and Figure 10 illustrate these definitions.

Substituting Eq. (144) into Eqs. (14) through (16), we get the principal moments of inertia for a center-beaded irregular tetrahedral star:

$$I_1 = 2mL^2[1 + 2\cos^2\theta_1]N_B(N_B + 1)(2N_B + 1) \quad (145)$$

$$I_2 = 2mL^2[1 + 2\cos^2\theta_1]N_B(N_B + 1)(2N_B + 1) = I_1 \quad (146)$$

$$I_3 = 4mL^2\sin^2\theta_1 N_B(N_B + 1)(2N_B + 1) \quad (147)$$

Substituting Eqs. (145) and (147) into Eqs. (21) through (23) gives the orientation constants for a center-beaded tetrahedral star branched polymer:

$$a \equiv \frac{N_B(N_B + 1)(2N_B + 1)}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35] \quad (148)$$

$$b \equiv \frac{3(3\cos^2\theta_1 - 1)^2}{5(\cos^2\theta_1 + 1)^2} = \frac{3(3\cos 2\theta_1 + 1)^2}{5(\cos 2\theta_1 + 3)^2} \quad (149)$$

$$v \equiv \frac{3}{[\cos 2\theta_1 + 2]N_B(N_B + 1)(2N_B + 1)} \quad (150)$$

where:

$$\frac{b}{v} = \frac{3(3\cos 2\theta_1 + 1)^2[\cos 2\theta_1 + 2]N_B(N_B + 1)(2N_B + 1)}{15(\cos 2\theta_1 + 3)^2} \quad (151)$$

Since $a < 0$ is unphysical, from Eq. (148) we learn that:

$$2\cos 2\theta_1 - 5\cos 4\theta_1 + 35 > 0 \quad (152)$$

which is always satisfied.

Multiplying a by v gives:

$$av = \frac{2\cos 2\theta_1 - 5\cos 4\theta_1 + 35}{5(\cos 2\theta_1 + 3)[\cos 2\theta_1 + 2]} \quad (153)$$

which, mindful of Eqs. (149) and (138), is a parametric function of b in θ_1 (see FIG 3 of [1]). Figure 11 illustrates, with Eqs. (153) and (149), how the macromolecular lopsidedness evolves with θ_1 . Figure 12 shows the progression in the $av - b$ plane of

the tetrahedral structures, starting with planar 4-arm stars (rightmost point on upper oblate branch) and progression leftward as θ_1 descends from $\frac{\pi}{2}$. From Figure 12, we discover that at $\theta_1 = \frac{1}{2}\theta_t$ the leftward progression jumps to the lower prolate branch, ending at:

$$b = \frac{3(3 \cos(\pi - \theta_t) + 1)^2}{5(\cos(\pi - \theta_t) + 3)^2} \quad (154)$$

where $\theta_1 = \frac{1}{2}(\pi - \theta_t)$, and where the 4-arm star is regular tetrahedral. Thus:

$$\frac{3(3 \cos(\pi - \theta_t) + 1)^2}{5(\cos(\pi - \theta_t) + 3)^2} \leq b \leq \frac{3}{5} \quad (155)$$

for tetrahedral macromolecules. When Eqs. (145) and (147) equate ($I_1 = I_3$), this gives:

$$\theta_1 = \frac{\pi}{3} \quad (156)$$

from which we learn that prolate tetrahedral macromolecules, from Eq. (138), range from:

$$\sin^{-1} \frac{d}{2L} \leq \theta_1 < \frac{\pi}{3} \quad (157)$$

and oblate:

$$\frac{\pi}{3} \leq \theta_1 \leq \frac{\pi}{2} \quad (158)$$

illustrated in Figure 12 (and **FIGS. 3** and **17** of [1]).

Inserting Eq. (150) into Eq. (31) yields:

$$\frac{\lambda}{\lambda_0} \equiv 4[\cos 2\theta_1 + 2]N_B(N_B + 1)(2N_B + 1) \quad (159)$$

for center-beaded tetrahedral stars.

Eqs. (148) through (150) are subject to Eq. (26). Substituting Eqs. (148) through (150) into Eqs. (45) and (46) yields, for suspensions of center-beaded tetrahedral star-branched polymers:

$$\frac{\eta' - \eta_s}{\eta_0 - \eta_s} = \frac{1 + \frac{6(3 \cos 2\theta_1 + 1)^2 [\cos 2\theta_1 + 2]}{[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35](\cos 2\theta_1 + 3)} \left(\frac{1}{1 + (\lambda\omega)^2} \right)}{1 + \frac{6(3 \cos 2\theta_1 + 1)^2 [\cos 2\theta_1 + 2]}{[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35](\cos 2\theta_1 + 3)}} \quad (160)$$

and:

$$\frac{\eta''}{\eta_0 - \eta_s} = \frac{\frac{6(3 \cos 2\theta_1 + 1)^2 [\cos 2\theta_1 + 2]}{[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35](\cos 2\theta_1 + 3)}}{1 + \frac{6(3 \cos 2\theta_1 + 1)^2 [\cos 2\theta_1 + 2]}{[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35](\cos 2\theta_1 + 3)}} \left\{ \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (161)$$

which we will recover, from time to time, below.

Substituting Eqs. (148) through (150) into Eqs. (49) and (40):

$$\frac{\eta'}{nkT\lambda_0} = 6 \frac{N_B(N_B + 1)(2N_B + 1)}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35] \left\{ 1 + \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (162)$$

and:

$$\frac{\eta''}{nkT\lambda_0} = 6 \frac{N_B(N_B + 1)(2N_B + 1)}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35] \left\{ \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]} \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (163)$$

as $\lambda\omega \rightarrow 0$:

$$\frac{\eta_0}{nkT\lambda_0} = 6 \frac{N_B(N_B + 1)(2N_B + 1)}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35] \left\{ 1 + \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]} \right\} \quad (164)$$

which we illustrate in Figure 13. We find the behaviour of Figure 13 to be intrinsically beautiful. Normalizing Eqs. (162) and (163) with Eq. (164) gives:

$$\frac{\eta'}{\eta_0} = \frac{1 + \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]} \left(\frac{1}{1 + (\lambda\omega)^2} \right)}{1 + \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]}} \quad (165)$$

and:

$$\frac{\eta''}{\eta_0} = \frac{\frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]} \frac{\lambda\omega}{1 + (\lambda\omega)^2}}{1 + \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]}} \quad (166)$$

We illustrate Eq. (165) for η' in Figure 14 (prolate) and Figure 15 (oblate), and Eq. (166) for η'' in Figure 16 (prolate) and Figure 17 (oblate). From Eq. (165), we then learn that for tetrahedral center-beaded star suspensions, from general rigid bead-rod theory, opening the interior angle of the tetrahedron decreases the real part of the complex viscosity. From Eq. (166), we then learn that for tetrahedral center-beaded star suspensions, from general rigid bead-rod theory, opening the interior angle of the tetrahedron increases the imaginary part of the complex viscosity.

To deepen our understanding of how branching affects the rheology of center-beaded tetrahedral stars ($N_A = 4$), we can normalize our main result, Eq. (164), with Eq. (4):

$$\frac{n^\ell \eta_0}{n\eta_0^\ell} = \frac{72N_B(N_B + 1)(2N_B + 1)}{N_A N_B (N_A N_B + 1)(N_A N_B + 2)} \left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{5(\cos 2\theta_1 + 3)^2} + \frac{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]}{5(\cos 2\theta_1 + 3)^2} \right\} \quad (167)$$

and Eq. (159) with Eq. (9):

$$\frac{\lambda}{\lambda^\ell} = \frac{24[\cos 2\theta_1 + 2]N_B(N_B + 1)(2N_B + 1)}{N_A N_B (N_A N_B + 1)(N_A N_B + 2)} \quad (168)$$

where the superscripted ℓ indicates unbranched.

b. CORELESS TETRAHEDRAL STARS ($N_A = 4$)

For coreless tetrahedral stars, Eq. (144) is subject to Eq. (84). Substituting Eq.(144) into Eqs. (14) through (16), we get the principal moments of inertia for a coreless irregular tetrahedral star:

$$I_1 = 2mL^2[1 + 2\cos^2\theta_1][-1 + N_B(N_B + 1)(2N_B + 1)] \quad (169)$$

$$I_2 = 2mL^2[1 + 2\cos^2\theta_1][-1 + N_B(N_B + 1)(2N_B + 1)] = I_1 \quad (170)$$

$$I_3 = 4mL^2\sin^2(\theta_1)[-1 + N_B(N_B + 1)(2N_B + 1)] \quad (171)$$

by *coreless*, we mean, the macromolecule lacks a center bead. Substituting Eqs. (169) through (171) into Eqs. (21) through (23) gives the orientation constants for a coreless tetrahedral star branched polymer:

$$a \equiv \frac{[-1 + N_B(N_B + 1)(2N_B + 1)]}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35] \quad (172)$$

$$b \equiv \frac{3(3 \cos 2\theta_1 + 1)^2}{5(\cos 2\theta_1 + 3)^2} \quad (173)$$

$$v \equiv \frac{3}{[\cos 2\theta_1 + 2][-1 + N_B(N_B + 1)(2N_B + 1)]} \quad (174)$$

Multiplying a by v gives at $\theta_1 = \pi/2$:

$$av = \frac{14}{5} \quad (175)$$

as it must, for $b = 3/5$ (see FIG 3 of [1]). Inserting Eq. (174) into Eq. (31) yields:

$$\frac{\lambda}{\lambda_0} \equiv 4[\cos 2\theta_1 + 2][-1 + N_B(N_B + 1)(2N_B + 1)] \quad (176)$$

for coreless tetrahedral stars.

Eqs. (172) through (174) are subject to Eq. (26). Substituting Eqs. (172) through (174) into Eqs. (45) and (46) yields, for suspensions of coreless tetrahedral star-branched polymers resulting in the same equations for $(\eta' - \eta_s)/(\eta_0 - \eta_s)$ and $\eta''/(\eta_0 - \eta_s)$ [Eqs. (160) and (161)] as center-beaded tetrahedral stars.

Substituting Eqs. (172) through (174) into Eqs. (49) and (40):

$$\frac{\eta'}{nkT\lambda_0} = 6 \frac{[-1 + N_B(N_B + 1)(2N_B + 1)]}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35] \left\{ 1 + \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (177)$$

and:

$$\frac{\eta''}{nkT\lambda_0} = 6 \frac{[-1 + N_B(N_B + 1)(2N_B + 1)]}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35] \left\{ \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]} \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (178)$$

as $\lambda\omega \rightarrow 0$:

$$\frac{\eta_0}{nkT\lambda_0} = 6 \frac{[-1 + N_B(N_B + 1)(2N_B + 1)]}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35] \left\{ 1 + \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]} \right\} \quad (179)$$

illustrated in Figure 13. Normalizing Eqs. (177) and (178) with Eq. (179) results in the same equations for η'/η_0 and η''/η_0 for center-beaded tetrahedral stars [Eqs. (165) and (166)], illustrated in Figure 14 (prolate) and Figure 15 (oblate) for η' , and in Figure 16 (prolate) and Figure 17 (oblate) for η'' .

To deepen our understanding of how branching affects the rheology of coreless tetrahedral stars ($N_A = 4$), we can normalize our main result, Eq. (164), with Eq. (4):

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{72[-1 + N_B(N_B + 1)(2N_B + 1)]}{N_A N_B (N_A N_B + 1)(N_A N_B + 2)} \left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{5(\cos 2\theta_1 + 3)^2} + \frac{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]}{5(\cos 2\theta_1 + 3)^2} \right\} \quad (180)$$

and Eq. (159) with Eq. (9):

$$\frac{\lambda}{\lambda^\ell} = \frac{24[\cos(2\theta_1) + 2][-1 + N_B(N_B + 1)(2N_B + 1)]}{N_A N_B (N_A N_B + 1)(N_A N_B + 2)} \quad (181)$$

where the superscripted ℓ indicates unbranched.

V. WORKED EXAMPLE: POLYBUTADIENE ($N_A = 4$)

In the following subsections of this worked example, we will test our main results for star-branched polymers by normalizing them with the well-known result for straight chains. We rely specifically on the measurements of [4] on the 4-arm star (sample ST1, Figure 18 and Figure 19) and on the corresponding straight chain (sample PBA, Figure 20 and Figure 21) of nearly the same molecular weight and of nearly the same and narrow polydispersity. Figure 22 displays the fit of Eq. (1) to the measured values of complex viscosity of sample PBA (Figs. 7.2 and 7.3 of [4]), and macromolecule illustrated in Figure 23, yielding $\eta_0 = 2.55 \times 10^3 \text{ Pa} \cdot \text{s}$ and $\lambda = 0.20 \text{ s}$ for the straight chain.

Fitting Eqs. (78) to the data from Fig. 7.10 of [4] yields Figure 24, we get $\eta_0 = 1.27 \times 10^5 \text{ Pa} \cdot \text{s}$ and $\lambda = 54.0 \text{ s}$ for a center-beaded or center-ringed planar 4-arm star. Thus we get (see Table 4):

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = 14.09 \quad (182)$$

from fitting general rigid bead-rod theory for center-beaded or center-ringed planar 4-arm star.

Fitting Eq. (165) to the data from Fig. 7.10 of [4], we get $\eta_0 = 1.38 \times 10^5 \text{ Pa} \cdot \text{s}$, $\lambda = 57.0 \text{ s}$, and $\theta_1 = 0.40 \text{ rad}$ for a center-beaded or coreless tetrahedral star (Figure 25). For these fitted values, Figure 26 then tests Eq. (166). From Figure 26, we learn that Eq. (166)

overpredicts the peak η'' and underpredicts its frequency. From the fitted values of Figure 25, for the center-beaded or coreless tetrahedral star, we get (see Table 4):

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = 15.31 \quad (183)$$

from fitting general rigid bead-rod theory for center-beaded or coreless tetrahedral star.

When you fit different structural formulas to the same η' data, you get different fitted values for η_0 , and thus different values for the scaled viscosity ratio $n^\ell \eta_0 / n \eta_0^\ell$. For instance, fitting reptation theory to the η' measurements of Figure 18 and Figure 20, Menezes gets $n^\ell \eta_0 / n \eta_0^\ell = 6.67$. By contrast, when we fit these same data from Eqs. (78) and (1) we get $n^\ell \eta_0 / n \eta_0^\ell = 14.09$ for center-beaded or center-ringed planar star.

a. COMPLEX VISCOSITY OF A CENTER-BEADED PLANAR STAR ($N_A = 4$)

Normalizing Eq. (77) with Eq. (1) gives Eq. (82), and when $N_A = 4$:

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{6(N_B + 1)}{4N_B + 1} \quad (184)$$

whose lower asymptote ($N_B \rightarrow \infty$) is $3/2$ and whose upper bound ($N_B \rightarrow 0$) is 6 as shown in Figure 27. This upper bound falls well below the measured value of 14.09 given in Eq. (182), from which we learn that branched polybutadiene of $[4,3]$ does not behave as center-beaded planar star.

b. COMPLEX VISCOSITY OF A CENTER-RINGED PLANAR STAR ($N_A = 4$)

Eq. (101) was normalized with Eq. (1), where $N_A = 4$, yielding:

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{6(N_B + 1)}{4N_B + 1} - \frac{6}{N_B(4N_B + 1)(2N_B + 1)} \quad (185)$$

whose upper bound ($N_B \rightarrow \infty$) is $3/2$ and whose lower bound ($N_B \rightarrow 0$) is $-\infty$, as shown in Figure 28. This upper bound falls well below the measured value of 14.09 given in Eq. (182), from which we learn that branched polybutadiene of $[4,3]$ does not behave as center-beaded planar star.

c. COMPLEX VISCOSITY OF A CENTER-BEADED TETRAHEDRAL STAR ($N_A = 4$)

Eq. (167) was normalized with Eq. (1), where $N_A = 4$, yielding:

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{9(N_B + 1)}{(4N_B + 1)} \left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2 + (\cos 2\theta_1 + 3)[2 \cos 2\theta_1 - 5 \cos 4\theta_1 + 35]}{5(\cos 2\theta_1 + 3)^2} \right\} \quad (186)$$

whose lower asymptote ($N_B \rightarrow \infty$) is:

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{9}{4} \left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2 + (\cos 2\theta_1 + 3)[2 \cos 2\theta_1 - 5 \cos 4\theta_1 + 35]}{5(\cos 2\theta_1 + 3)^2} \right\} \quad (187)$$

and whose upper bound ($N_B \rightarrow 0$) is:

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = 9 \left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2 + (\cos 2\theta_1 + 3)[2 \cos 2\theta_1 - 5 \cos 4\theta_1 + 35]}{5(\cos 2\theta_1 + 3)^2} \right\} \quad (188)$$

as shown in Figure 29. The measured value of 15.31 given in Eq. (183) falls within these bounds, from which we learn that branched polybutadiene of [4, 3] behaves as an irregular center-beaded tetrahedral star at $\theta_1 = 0.40$ rad (23°), giving:

$$N_B = 0.147 \quad (189)$$

from which we learn that, for 4-arm polybutadiene stars of molecular weight 200,000 g/gmol, this non-integer value obtains. Thus, $N_B = 1$ corresponds to 1,360,000 g/gmol, and so N_B will only be discrete for multiples of 1,360,000 g/gmol. Figure 30 illustrates the irregular tetrahedron with $\theta_1 = 0.40$ rad for a 4-arm polybutadiene star of molecular weight 4,080,000 g/gmol ($N_B = 3$). Since $\theta_1 = 0.40$ rad, we find that 4-arm polybutadiene star complex viscosity behaviour is nearer the regular tetrahedron [$\theta_1 = \frac{1}{2}(\pi - \theta_t)$] than the planar polygon ($\theta_1 = \frac{\pi}{2}$).

We thus find our general rigid bead-rod theory that most closely follows the measured complex viscosity behaviour of the 4-arm star-branched polybutadiene solution is of the irregular center-beaded tetrahedral star at $\theta_1 = 0.40$ rad. We know that the specific 4-arm star-branched polybutadiene examined herein, has a silicon atom (and thus silicon tetrahedral bonding) at its core (**Table I** of [19]). Silicon bonding is regular tetrahedral, thus with $\theta_1 = \frac{1}{2}(\pi - \theta_t)$ rad = 0.62 rad [20,21,22], which is just above $\theta_1 = 0.40$ rad. In other words, in oscillatory shear flow, our 4-arm star-branched polybutadiene solution behaviour is nearly tetrahedral, and specifically, just 0.22 rad (12°) on the prolate side of regular tetrahedral. So our 4 polybutadiene arms emanate nearly tetrahedrally from their silicon central core linking atom.

We next turn our attention to the Cole-Cole plots for which **FIG. 1** of [23] applies where, for the center-beaded 4-arm star, b/v is given by Eq. (151). Specifically, for $\theta_1 = 0.40$ rad and $N_B = 0.147$ [from Eq. (189)], we get $b/v = 0.0822$. Plotting the complex viscosity measurements of Fig. 3 of [3] (or Fig. 7.10 of [4]) as a parametric plot in $\lambda\omega$ for $b/v = 0.0822$ yields Figure 31. From Figure 31, we learn that unlike for long-chain branching in molten polypropylene, general rigid bead-rod theory does not predict the Cole-Cole behaviour of star-branched polybutadiene solution accurately (compare Figure 31 with the good agreement in **FIG. 18** of [23]).

d. COMPLEX VISCOSITY OF A CORELESS TETRAHEDRAL STAR ($N_A = 4$)

Eq. (179) was normalized with Eq. (1), where $N_A = 4$, yielding:

$$\begin{aligned} \frac{n^\ell \eta_0}{n \eta_0^\ell} &= \frac{9[-1 + N_B(N_B + 1)(2N_B + 1)]}{N_B(4N_B + 1)(2N_B + 1)} \left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2 + (\cos 2\theta_1 + 3)[2 \cos 2\theta_1 - 5 \cos 4\theta_1 + 35]}{5(\cos 2\theta_1 + 3)^2} \right\} \quad (190) \end{aligned}$$

whose upper bound ($N_B \rightarrow \infty$) is:

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{9}{4} \left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2 + (\cos 2\theta_1 + 3)[2 \cos 2\theta_1 - 5 \cos 4\theta_1 + 35]}{5(\cos 2\theta_1 + 3)^2} \right\} \quad (191)$$

and whose lower bound ($N_B \rightarrow 0$) is:

$$\frac{n^\ell \eta_0}{n \eta_0^\ell} = -\infty \quad (192)$$

as shown in Figure 32. This upper bound falls well below the measured value of 14.59 given in Eq. (183), from which we learn that branched polybutadiene of [4, 3] does not behave as coreless tetrahedral star.

VI. CONCLUSION

We arrive at the general expressions for the real and imaginary parts of the complex viscosity for planar stars of any number of branches or branch length for both center-beaded [Eqs. (78) and (79)] and center-ringed [Eqs. (78) and (79)]. We find these planar predictions to disagree with the measured complex viscosity behaviour of the polybutadiene solutions. We thus next arrive at the general expressions for the real and imaginary parts of the complex viscosity for tetrahedral stars of any branch length or interior angle for both center-beaded [Eqs. (165) and (166)] and coreless [Eqs. (165) and (166)]. We find the measured complex viscosity behaviour of polybutadiene solutions, one quadrafunctional star-branched, the other unbranched, of the same molecular weight ($M_w = 200,000$ g/gmol) to agree with the predictions of general rigid bead-rod theory (Figure 25). Specifically, we learn that when general rigid bead-rod theory is applied to our quadrafunctional polybutadiene, a slightly irregular center-beaded tetrahedron of interior angle 134° is required (with 1,360,000 g/gmol per bead) to describe accurately the real part of its complex viscosity behaviour (see Figure 30). This is consistent with its silicon centered (and thus tetrahedral) chemistry (see Figure 33 and Figure 34). However, this same general rigid bead-rod theory overpredicts the peak of the imaginary part of its complex viscosity, and underpredicts the peak frequency (see Figure 26). We attribute this discrepancy to branch length dispersity, be it from branch-to-branch on the same star or between stars. To handle such mixtures of different species we can rewrite Eqs. (165) and (166) for a dispersed system of S species (see Problem 14C.2 of [5], see also Sec. 26 of [17]). We leave this for another day.

Our work on tetrahedral stars uncovers a new pair of dumbbells: the 5-bead or 4-bead quarter-twisted osculated dumbbells shown respectively in Figure 35 and Figure 36. For these we subject Eqs. (165) and (166) to the osculation constraint $\sin \theta_1 = d/2L$. We also leave this exploration for another day.

From Figure 11, we learnt that the lopsidedness of tetrahedral macromolecules, $2b/av$, versus θ_1 is curiously asymmetric. With some effort, employing Eqs. (153) and (149), we can transform the function illustrated in Figure 11 to a Fourier series. We leave this task for another day.

We observe that recent work on ancient polymers transported by meteorites may also be 4-arm stars of structures more complex than our tetrahedral polybutadienes (FIG. 9 of [24]). Called *stacked tetraskelia*, we leave the evaluation of their complex viscosity in solution, from first principles and of the method of general rigid bead-rod theory for another day.

When using the references cited herein, it is best to be mindful of corresponding ganged errata in [25].

VII. DATA AVAILABILITY

The data that support the findings of this study are available within the article.

VIII. ACKNOWLEDGMENT

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Table 1: Literature on general formulas for planar macromolecules (TABLE XV of [1]).

Macromolecule	$\frac{l_1}{mL^2}, \frac{l_2}{mL^2}$	$\frac{l_3}{mL^2}$	a	b	ν	$\frac{2b}{a\nu}$	$\frac{\eta_0 - \eta_s}{nkT\lambda}$	$\frac{\lambda}{\lambda_0}$	$\frac{\Psi_{1,0}}{\lambda(\eta_0 - \eta_s)}$
Shish-kebab of N beads	$\frac{1}{12}N(N^2 - 1)$	0	$\frac{1}{90}N(N^2 - 1)$	$\frac{3}{5}$	$\frac{72}{N(N^2 - 1)}$	$\frac{3}{2}$	1	$\frac{1}{6}N(N^2 - 1)$	$\frac{6}{5}$
Rigid rings of N beads	$\frac{N}{8 \sin^2 \frac{\pi}{N}}$	$\frac{N}{4 \sin^2 \frac{\pi}{N}}$	$\frac{7N}{120 \sin^2 \frac{\pi}{N}}$	$\frac{3}{5}$	$\frac{48}{N} \sin^2 \frac{\pi}{N}$	$\frac{3}{7}$	2	$\frac{N}{4 \sin^2 \frac{\pi}{N}}$	$\frac{3}{5}$
Star-branched polymers with $N - 1$ branches and N beads ($4 \leq N \leq 7$)	$\frac{N - 1}{2}$	$N - 1$	$\frac{7}{30}(N - 1)$	$\frac{3}{5}$	$\frac{12}{N - 1}$	$\frac{3}{7}$	2	$N - 1$	$\frac{3}{5}$
Star-branched polymers with $N - 1$ branches and N beads ($N \geq 8$)	$\frac{N - 1}{8 \sin^2 \frac{\pi}{N - 1}}$	$\frac{N - 1}{4 \sin^2 \frac{\pi}{N - 1}}$	$\frac{7(N - 1)}{120 \sin^2 \frac{\pi}{N - 1}}$	$\frac{3}{5}$	$\frac{48}{N - 1} \sin^2 \frac{\pi}{N - 1}$	$\frac{3}{7}$	2	$\frac{N - 1}{4 \sin^2 \frac{\pi}{N - 1}}$	$\frac{3}{5}$

Table 2: Dimensional Variables.

Name	Symbol	Dimensions
Angular frequency	ω	t^{-1}
Bead center to center length of rigid dumbbell	L	L
Bead diameter	d	L
Bead friction coefficient	ξ	M/t
Bead position for irregular tetrad, spherical coordinates	θ_1	rad
Branch angle	θ_n	$1 \leq n \leq N_A$
Cartesian coordinates	x, y, z	L
Cartesian coordinates with respect to the center of mass	$\hat{\delta}_1, \hat{\delta}_2, \hat{\delta}_3$	L
Complex viscosity	η^*	M/Lt
Complex viscosity, real part	η'	M/Lt
Complex viscosity, <i>minus</i> imaginary part	η''	M/Lt
Element for Kronecker Delta	$\delta(s)$	t^{-1}
Energy values in molecular-scale systems	kT	ML^2/t^2
First normal stress coefficient, small amplitude oscillatory shear response, displacement term	Ψ_1^d, Ψ_2^d	M/L
First/second normal stress coefficient, in-phase with $\cos 2\omega t$, for small amplitude oscillatory shear response	Ψ_1', Ψ_2'	M/L
First/second normal stress coefficient, out-of-phase with $\cos 2\omega t$, for small amplitude oscillatory shear response	Ψ_1'', Ψ_2''	M/L
First/second normal stress coefficient, complex	Ψ_1^*, Ψ_2^*	M/L
Macromolecular center of mass	$\mathbf{R}$	L
Mass of each bead	m_i	M
Molecular weight	M_w	M/mole
Moments of inertia	I_1, I_2, I_3	ML^2
Normal stress differences	$\tau_{21}, \tau_{11}, \tau_{22}, \tau_{33}$	M/Lt^2
Number of dumbbells per unit volume	n	$1/L^3$
Number of dumbbells per unit volume, unbranched chain	n^ℓ	$1/L^3$

Polymer contribution to the extra stress tensor	$\boldsymbol{\tau}_p$	M/Lt^2
Position vector of the i th bead with respect to the center of mass	$\mathbf{R}_i$	L
Position vector with respect to the center of mass for each bead of a planar star on the n th arm	$\mathbf{R}_{n,c}$	L
Position vector of the i th bead	$\mathbf{r}_i$	L
Relaxation time of a rigid dumbbell	λ_0	t
Relaxation time of solution	λ	t
Relaxation time of unbranched solution	λ^ℓ	t
Spherical coordinates	r, θ, ϕ	rad
Shear rate amplitude	$\dot{\gamma}^0$	t^{-1}
Shear rate at specific time	$\dot{\gamma}(t')$	t^{-1}
Shear rate tensor	$\dot{\boldsymbol{\gamma}}(t)$	t^{-1}
Shear rate	$\dot{\gamma}(t)$	t^{-1}
Shear relaxation function	$G(s)$	M/Lt^2
Tetrahedral angle	Θ_t	rad
Time, past	t'	t
Time, current	t	t
Time, past time interval	$s \equiv t - t'$	t
Total mass	M	M
Velocity vector	$\mathbf{v}$	L/t
Viscosity, solvent	η_s	M/Lt
Viscosity, zero shear of real part	η_0	M/Lt
Viscosity, zero shear of <i>minus</i> imaginary part	η_0''	M/Lt
Viscosity, zero shear of linear macromolecules	η_0^ℓ	M/Lt
Viscosity, real part at high frequency	η_∞'	M/Lt
Viscosity, <i>minus</i> imaginary part at high frequency	η_∞''	M/Lt

Legend: $M \equiv$ mass, $L \equiv$ length, $t \equiv$ time, rad $\equiv$ radian

Table 3: Dimensionless Variables and Groups.

Name	Symbol	Range
Architectural constants	a, b, ν	> 0
Arm number	n	≥ 0
Bead number along each branch	c	≥ 0
Bead volume fraction	φ	≥ 0
Concertation factor	$\frac{n^\ell \eta_0}{n \eta_0^\ell}$	> 0
Coefficient in Eqs. (56) through (58)	Z, α, β	≥ 0
Coefficients in Eqs. (105) through (107)	α_c, β_c	≥ 0
Deborah number	$\lambda \omega$	≥ 0
Lopsidedness	$2b/av$	> 0
Number of arms on the macromolecules	N_A	≥ 0
Number of beads on each arm on the macromolecule	N_B	≥ 0
Total number of beads	N	> 0

Table 4: Polybutadiene Solution Properties

PBA	ST1 – Planar	ST1 – Tetrahedral
$\eta_0^\ell = 2.55 \times 10^3 \text{ Pa} \cdot \text{s}$	$\eta_0 = 1.27 \times 10^5 \text{ Pa} \cdot \text{s}$	$\eta_0 = 1.38 \times 10^5 \text{ Pa} \cdot \text{s}$
$\lambda^\ell = 0.2 \text{ s}$	$\lambda = 5.40 \times 10^1 \text{ s}$	$\lambda = 5.70 \times 10^1 \text{ s}$
$n^\ell = 0.0676 \text{ g/cm}^3$	$n = 0.239 \text{ g/cm}^3$	$n = 0.239 \text{ g/cm}^3$

Table 5: Analytical Results – Planar $3 \leq N_A \leq 6$

Center-beaded	Center-ringed
$I_1 \equiv \frac{N_A}{2} N_B(N_B + 1)(2N_B + 1)mL^2$	$I_1 \equiv mL^2[-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{2}$
$I_2 \equiv \frac{N_A}{2} N_B(N_B + 1)(2N_B + 1)mL^2 = I_1$	$I_2 \equiv mL^2[-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{2}$ $= I_1$
$I_3 \equiv N_A N_B(N_B + 1)(2N_B + 1)mL^2$	$I_3 \equiv mL^2[-1 + N_B(N_B + 1)(2N_B + 1)]N_A$
$a \equiv \frac{7}{30} N_A N_B(N_B + 1)(2N_B + 1)$	$a \equiv \frac{7}{30} [-1 + N_B(N_B + 1)(2N_B + 1)]N_A$
$b \equiv \frac{3}{5}$	$b \equiv \frac{3}{5}$
$v \equiv \frac{12}{N_A N_B(N_B + 1)(2N_B + 1)}$	$v \equiv \frac{12}{[-1 + N_B(N_B + 1)(2N_B + 1)]N_A}$
$\frac{\lambda}{\lambda_0} \equiv N_A N_B(N_B + 1)(2N_B + 1)$	$\frac{\lambda}{\lambda_0} \equiv N_A[-1 + N_B(N_B + 1)(2N_B + 1)]$
$\frac{\eta_0}{nkT\lambda_0} = 2N_A N_B(N_B + 1)(2N_B + 1)$	$\frac{\eta_0}{nkT\lambda_0} = 2[-1$ $+ N_B(N_B + 1)(2N_B + 1)]N_A$
$\frac{\eta'}{\eta_0} = \frac{7}{10} \left\{ 1 + \frac{3}{7} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\}$	
$\frac{\eta''}{\eta_0} = \frac{3}{10} \left\{ \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\}$	
$\frac{n^\ell \eta_0}{n\eta_0^\ell} = \frac{12(N_B + 1)(2N_B + 1)}{(N_A N_B + 1)(N_A N_B + 2)}$	$\frac{n^\ell \eta_0}{n\eta_0^\ell} = \frac{12(N_B + 1)(2N_B + 1)}{(N_A N_B + 1)(N_A N_B + 2)}$ $\frac{12}{N_B(N_A N_B + 1)(N_A N_B + 2)}$
$\frac{\lambda}{\lambda^\ell} = \frac{6(N_B + 1)(2N_B + 1)}{(N_A N_B + 1)(N_A N_B + 2)}$	$\frac{\lambda}{\lambda^\ell} = \frac{6(N_B + 1)(2N_B + 1)}{(N_A N_B + 1)(N_A N_B + 2)}$ $\frac{6}{N_B(N_A N_B + 1)(N_A N_B + 2)}$

Table 6: Analytical Results – Planar $N_A \geq 7$

Center-beaded	Center-ringed
$I_1 \equiv \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}} N_B(N_B + 1)(2N_B + 1)mL^2$	$I_1 \equiv mL^2[-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}}$
$I_2 \equiv \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}} N_B(N_B + 1)(2N_B + 1)mL^2$ $= I_1$	$I_2 \equiv mL^2[-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{8 \sin^2 \frac{\pi}{N_A}} = I_1$
$I_3 \equiv \frac{N_A}{4 \sin^2 \frac{\pi}{N_A}} N_B(N_B + 1)(2N_B + 1)mL^2$	$I_3 \equiv mL^2[-1 + N_B(N_B + 1)(2N_B + 1)] \frac{N_A}{4 \sin^2 \frac{\pi}{N_A}}$
$a \equiv \frac{7}{120 \sin^2 \frac{\pi}{N_A}} N_A N_B(N_B + 1)(2N_B + 1)$	$a \equiv \frac{7}{120 \sin^2 \frac{\pi}{N_A}} [-1 + N_B(N_B + 1)(2N_B + 1)] N_A$
$b \equiv \frac{3}{5}$	$b \equiv \frac{3}{5}$
$v \equiv \frac{48 \sin^2 \frac{\pi}{N_A}}{N_A N_B(N_B + 1)(2N_B + 1)}$	$v \equiv \frac{48 \sin^2 \frac{\pi}{N_A}}{[-1 + N_B(N_B + 1)(2N_B + 1)] N_A}$
$\frac{\lambda}{\lambda_0} \equiv \frac{N_A N_B(N_B + 1)(2N_B + 1)}{4 \sin^2 \frac{\pi}{N_A}}$	$\frac{\lambda}{\lambda_0} \equiv \frac{[-1 + N_B(N_B + 1)(2N_B + 1)] N_A}{4 \sin^2 \frac{\pi}{N_A}}$
$\frac{\eta_0}{nkT\lambda_0} = \frac{1}{2 \sin^2 \frac{\pi}{N_A}} N_A N_B(N_B + 1)(2N_B + 1)$	$\frac{\eta_0}{nkT\lambda_0} = \frac{1}{2 \sin^2 \frac{\pi}{N_A}} [-1 + N_B(N_B + 1)(2N_B + 1)] N_A$
$\frac{\eta'}{\eta_0} = \frac{7}{10} \left\{ 1 + \frac{3}{7} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\}$	
$\frac{\eta''}{\eta_0} = \frac{3}{10} \left\{ \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\}$	

Table 7: Analytical Results – Tetrahedral

Center-beaded		Coreless	
$I_1 = 2mL^2[1 + 2\cos^2\theta_1]N_B(N_B + 1)(2N_B + 1)$		$I_1 = 2mL^2[1 + 2\cos^2\theta_1][-1 + N_B(N_B + 1)(2N_B + 1)]$	
$I_2 = 2mL^2[1 + 2\cos^2\theta_1]N_B(N_B + 1)(2N_B + 1) = I_1$		$I_2 = 2mL^2[1 + 2\cos^2\theta_1][-1 + N_B(N_B + 1)(2N_B + 1)] = I_1$	
$I_3 = 4mL^2\sin^2\theta_1 N_B(N_B + 1)(2N_B + 1)$		$I_3 = 4mL^2\sin^2(\theta_1)[-1 + N_B(N_B + 1)(2N_B + 1)]$	
$a \equiv \frac{N_B(N_B + 1)(2N_B + 1)}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]$		$a \equiv \frac{[-1 + N_B(N_B + 1)(2N_B + 1)]}{15(\cos 2\theta_1 + 3)} [2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]$	
$b \equiv \frac{3(3 \cos^2\theta_1 - 1)^2}{5(\cos^2\theta_1 + 1)^2} = \frac{3(3 \cos 2\theta_1 + 1)^2}{5(\cos 2\theta_1 + 3)^2}$			
$\nu \equiv \frac{3}{[\cos 2\theta_1 + 2]N_B(N_B + 1)(2N_B + 1)}$		$\nu \equiv \frac{3}{[\cos 2\theta_1 + 2][-1 + N_B(N_B + 1)(2N_B + 1)]}$	
$\frac{\lambda}{\lambda_0} \equiv 4[\cos(2\theta_1) + 2]N_B(N_B + 1)(2N_B + 1)$		$\frac{\lambda}{\lambda_0} \equiv 4[\cos(2\theta_1) + 2][-1 + N_B(N_B + 1)(2N_B + 1)]$	
$\frac{\eta_0}{n_k T \lambda_0} = 6 \frac{N_B(N_B + 1)(2N_B + 1)}{15(\cos(2\theta_1) + 3)} [2\cos(2\theta_1) - 5\cos(4\theta_1) + 35] \left\{ 1 + \frac{6[\cos(2\theta_1) + 2](3 \cos(2\theta_1) + 1)^2}{(\cos(2\theta_1) + 3)[2\cos(2\theta_1) - 5\cos(4\theta_1) + 35]} \right\}$		$\frac{\eta_0}{n_k T \lambda_0} = 6 \frac{[-1 + N_B(N_B + 1)(2N_B + 1)]}{15(\cos(2\theta_1) + 3)} [2\cos(2\theta_1) - 5\cos(4\theta_1) + 35] \left\{ 1 + \frac{6[\cos(2\theta_1) + 2](3 \cos(2\theta_1) + 1)^2}{(\cos(2\theta_1) + 3)[2\cos(2\theta_1) - 5\cos(4\theta_1) + 35]} \right\}$	
$\frac{\eta'}{\eta_0} = \frac{1 + \frac{6[\cos(2\theta_1) + 2](3 \cos(2\theta_1) + 1)^2}{(\cos(2\theta_1) + 3)[2\cos(2\theta_1) - 5\cos(4\theta_1) + 35]}}{1 + \frac{6[\cos(2\theta_1) + 2](3 \cos(2\theta_1) + 1)^2}{(\cos(2\theta_1) + 3)[2\cos(2\theta_1) - 5\cos(4\theta_1) + 35]}} \left(\frac{1}{1 + (\lambda\omega)^2} \right)$			
$\frac{\eta''}{\eta_0} = \frac{1 + \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]}}{1 + \frac{6[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{(\cos 2\theta_1 + 3)[2\cos 2\theta_1 - 5\cos 4\theta_1 + 35]}} \frac{\lambda\omega}{1 + (\lambda\omega)^2}$			

$\frac{n^\ell \eta_0}{m\eta_0^\ell} = \frac{72N_B(N_B + 1)(2N_B + 1)}{N_A N_B (N_A N_B + 1)(N_A N_B + 2)}$	$\left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{+ (\cos 2\theta_1 + 3) \left[\frac{2 \cos 2\theta_1}{-5 \cos 4\theta_1 + 35} \right]} \right\}$	$\frac{n^\ell \eta_0}{m\eta_0^\ell} = \frac{72[-1 + N_B(N_B + 1)(2N_B + 1)]}{N_A N_B (N_A N_B + 1)(N_A N_B + 2)}$	$\left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2}{+ (\cos 2\theta_1 + 3) \left[\frac{2 \cos 2\theta_1}{-5 \cos 4\theta_1 + 35} \right]} \right\}$
$\frac{\lambda}{\lambda^\ell} = \frac{24[\cos(2\theta_1) + 2]N_B(N_B + 1)(2N_B + 1)}{N_A N_B (N_A N_B + 1)(N_A N_B + 2)}$		$\frac{\lambda}{\lambda^\ell} = \frac{24[\cos(2\theta_1) + 2][-1 + N_B(N_B + 1)(2N_B + 1)]}{N_A N_B (N_A N_B + 1)(N_A N_B + 2)}$	

Table 8: Worked Example ($N_A = 4$).

Macromolecule Structure	Concentration Factor
Center-Beaded Planar Star	$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{6(N_B + 1)}{4N_B + 1}$
Center-Ringed Planar Star	$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{6(N_B + 1)}{4N_B + 1} - \frac{6}{N_B(4N_B + 1)(2N_B + 1)}$
Center-Beaded Tetrahedral Star	$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{9(N_B + 1)}{(4N_B + 1)} \left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2 + (\cos 2\theta_1 + 3)[2 \cos 2\theta_1 - 5 \cos 4\theta_1 + 35]}{5(\cos 2\theta_1 + 3)^2} \right\}$
Coreless Tetrahedral Star	$\frac{n^\ell \eta_0}{n \eta_0^\ell} = \frac{9[-1 + N_B(N_B + 1)(2N_B + 1)]}{N_B(4N_B + 1)(2N_B + 1)} \left\{ \frac{[\cos 2\theta_1 + 2](3 \cos 2\theta_1 + 1)^2 + (\cos 2\theta_1 + 3)[2 \cos 2\theta_1 - 5 \cos 4\theta_1 + 35]}{5(\cos 2\theta_1 + 3)^2} \right\}$

Figure 1: Defining L for a 3-bead shish-kebab.

Figure 2: Defining L when $3 \leq N_A \leq 6$ in a center-beaded planar star-branched macromolecule. Specific example $N_A = 4$, $N_B = 2$.

Figure 3: Defining L when $3 \leq N_A \leq 6$ in a center-ringed planar star-branched macromolecule. Specific example $N_A = 4$, $N_B = 3$.

Figure 4: Defining L when $N_A \leq 7$ center-beaded planar star-branched macromolecule. Specific example $N_A = 8$, $N_B = 2$.

Figure 5: Defining L when $N_A \leq 7$ center-ringed planar star-branched macromolecule. Specific example $N_A = 8$, $N_B = 3$.

Figure 6: $\eta'/\eta_0(\lambda\omega)$ from Eq. (78) for center-beaded and center-ringed planar stars.

Figure 7: $\eta''/\eta_0(\lambda\omega)$ from Eq. (79) for center-beaded and center-ringed planar stars.

Figure 8: Molecular coordinates installed on 4-arm star. Specific example of center-beaded regular tetrahedral star ($\theta_1 = \frac{1}{2}\theta_t$) with $N_B = 2$. Spherical coordinates follow **Fig. A.8-2** of [18].

Figure 9: Defining L for center-beaded regular tetrahedral star-branched macromolecule. Specific example: $N_A = 4$, $N_B = 2$. $\mathbf{R}_i$ given by Eq. (144) with $\theta_1 = \frac{1}{2}(\pi - \theta_t)$ and $c = 1, \dots, N_B$.

Figure 10: Bead location for determining L for coreless regular tetrahedral star-branched macromolecule. Specific example: $N_A = 4$, $N_B = 2$. $\mathbf{R}_i$ given by Eq. (144) with $\theta_1 = \frac{1}{2}\theta_t$ and $c = 1, \dots, N_B$.

Figure 11: $2b/av$ versus θ_1 for tetrahedral macromolecules, both regular and irregular. av and b , given by Eqs. (153) and (149) (Eqs. (22) and (23) of [1]), are parametric in θ_1 over the range Eq. (138). The interior angle of the tetrahedra decreases with θ_1 .

Figure 12: av versus b for tetrahedral macromolecules, both regular and irregular. av and b , given by Eqs. (153) and (149) (Eqs. (22) and (23) of [1]), are parametric in θ_1 over the range Eq. (138). The oblate branch (top, right to left) has macromolecules of $\theta_1 = \frac{\pi}{2}$ rad and 1.3 rad and for the prolate branch (bottom, left to right) has macromolecules of $\theta_1 = \frac{\theta_t}{2}$ rad, $\theta_1 = 0.90$ rad, $\theta_1 = \frac{1}{2}(\pi - \theta_t)$ rad, and $\theta_1 = 0.40$ rad.

Figure 13: $N_B(N_B + 1)(2N_B + 1)\eta_0/nkT\lambda_0$ and $[-1 + N_B(N_B + 1)(2N_B + 1)]\eta_0/nkT\lambda_0$ versus θ_1 from Eqs. (164) and (179) for center-beaded and coreless tetrahedral stars.

Figure 14: $\eta'/\eta_0(\lambda\omega)$ from Eq. (165) for center-beaded and coreless tetrahedral stars at varying θ_1 for prolate macromolecules [Eq. (157)] [Black: $\theta_1 = \frac{1}{2}\theta_t$; Magenta: $\theta_1 = 0.90$ rad; Cyan: $\theta_1 = 0.80$ rad; Blue: $\theta_1 = \frac{1}{2}(\pi - \theta_t)$ rad; Green: $\theta_1 = 0.40$ rad; Yellow: $\theta_1 = 0.20$ rad; Red: $\theta_1 = 0.0$ rad].

Figure 15: $\eta'/\eta_0(\lambda\omega)$ from Eq. (165) for center-beaded and coreless tetrahedral stars at varying θ_1 for oblate macromolecules [Eq. (158)] [Black: $\theta_1 = \frac{1}{2}\pi$; Magenta: $\theta_1 = 1.5$ rad; Cyan: $\theta_1 = 1.4$ rad; Blue: $\theta_1 = 1.3$ rad; Green: $\theta_1 = 1.2$ rad; Yellow: $\theta_1 = 1.1$ rad; Red: $\theta_1 = \frac{1}{3}\pi$].

Figure 16: $\eta''/\eta_0(\lambda\omega)$ from Eq. (166) for center-beaded and coreless tetrahedral stars at varying θ_1 for prolate macromolecules [Eq. (157)] [Black: $\theta_1 = \frac{1}{2}\theta_t$; Magenta: $\theta_1 = 0.90$ rad; Cyan: $\theta_1 = 0.80$ rad; Blue: $\theta_1 = \frac{1}{2}(\pi - \theta_t)$ rad; Green: $\theta_1 = 0.40$ rad; Yellow: $\theta_1 = 0.20$ rad; Red: $\theta_1 = 0.0$ rad].

Figure 17: $\eta''/\eta_0(\lambda\omega)$ from Eq. (166) for center-beaded and coreless tetrahedral stars at varying θ_1 for oblate macromolecules [Eq. (158)] [Black: $\theta_1 = \frac{1}{2}\pi$; Magenta: $\theta_1 = 1.5$ rad; Cyan: $\theta_1 = 1.4$ rad; Blue: $\theta_1 = 1.3$ rad; Green: $\theta_1 = 1.2$ rad; Yellow: $\theta_1 = 1.1$ rad; Red: $\theta_1 = \frac{1}{3}\pi$].

Figure 18: Experimental $\eta'(\omega)$ data for sample ST1 from [4,3].

Figure 19: Experimental $\eta''(\omega)$ data for sample ST1 from [4,3].

Figure 20: Experimental $\eta'(\omega)$ data for sample PBA from [4,3].

Figure 21: Experimental $\eta''(\omega)$ data for sample PBA from [4,3].

Figure 22: η'/η_0^ℓ from Eq. (5) for unbranched fitted to data for straight chain in Figure 20 ($\lambda = 0.2$ s, $\eta_0 = 2.55 \times 10^3$ Pa s).

Figure 23: Results for unbranched polybutadiene sample (PBA) explained with a 4-bead shish-kebab.

Figure 24: $\eta'/\eta_0(\lambda\omega)$ from Eq. (78) for center-beaded and center-ringed planar star fitted to data for 4-arm star in Figure 18 ($\eta_0 = 1.27 \times 10^5 \text{ Pa s}$ and $\lambda = 54.0 \text{ s}$).

Figure 25: $\eta'/\eta_0(\lambda\omega)$ from Eq. (165) for center-beaded and center-ringed tetrahedral star at varying θ_1 for prolate macromolecules [Eq. (157)] [Black: $\theta_1 = \frac{1}{2}\theta_t$; Magenta: $\theta_1 = 0.90$ rad; Cyan: $\theta_1 = 0.80$ rad; Blue: $\theta_1 = \frac{1}{2}(\pi - \theta_t)$ rad; Green: $\theta_1 = 0.40$ rad; Yellow: $\theta_1 = 0.20$ rad; Red: $\theta_1 = 0.0$ rad] fitted to data for 4-arm star in Figure 18 ($\eta_0 = 1.38 \times 10^5$ Pa s and $\lambda = 57.0$ s).

Figure 26: $\eta''/\eta_0(\lambda\omega)$ from Eq. (166) for center-beaded and coreless tetrahedral stars at $\theta_1 = 0.40$ rad (prolate) for fitted values for 4-arm star of Figure 25 ($\eta_0 = 1.38 \times 10^5$ Pa s and $\lambda = 57.0$ s).

Figure 27: $n^l \eta_0 / n \eta_0^l$ from Eq. (184) for center-beaded planar stars for 4-arm stars with varying branch length ($\eta_0 = 1.27 \times 10^5$ Pa s and $\lambda = 54.0$ s).

Figure 28: $n^\ell \eta_0 / n \eta_0^\ell$ from Eq. (185) for center-ringed planar stars for 4-arm stars with varying branch length ($\eta_0 = 1.27 \times 10^5$ Pa s and $\lambda = 54.0$ s).

Figure 29: $n^\ell \eta_0 / n \eta_0^\ell$ from Eq. (186) for center-beaded tetrahedral stars at $\theta_1 = 0.40$ for 4-arm stars with varying branch length ($\eta_0 = 1.38 \times 10^5$ Pa s, $\lambda = 57.0$ s).

Figure 30: Results for star-branched polybutadiene sample (ST1) explained with a 4-arm irregular center-beaded tetrahedral: $N_A = 4$, and $N_B = 3$ for $M_w = 4.08 \times 10^6$ g/gmol. $\mathbf{R}_i$ given by Eq. (144) with $\theta_1 = 0.40$ rad = 23° and $c = 1, \dots, N_B$.

Figure 31: Fit of dimensionless Cole-Cole plot of Eq. (62) of [23] for center-beaded polybutadiene for tetrahedral stars with $\theta_1 = 0.40$, $N_B = 0.147$, and $b/\nu = 0.0822$ ($\eta_0 = 1.38 \times 10^5$ Pa s, $\lambda = 57.0$ s).

Figure 32: $n^l \eta_0 / n \eta_0^l$ from Eq. (186) for coreless tetrahedral stars at $\theta_1 = 0.40$ for 4-arm stars with varying branch length ($\eta_0 = 1.38 \times 10^5$ Pa s, $\lambda = 57.0$ s).

Figure 33: Space filling representation with Skeletal Structural Formula [26] inset of silicon linked 4-arm tetrahedral *cis*-polybutadiene star ($N_A = 4$) with its first 4 *cis* isomers ($M_w = 192.38$ g/gmol) produced by lithium catalyzed anionic polymerization followed by silicon chloride linking [4,20,21,3].

Figure 34: Space filling representation with Skeletal Structural Formula [26] inset of silicon tetrachloride linked 4-arm tetrahedral *trans*-polybutadiene star ($N_A = 4$) with its first 4 *trans* isomers ($M_w = 248.49$ g/gmol) produced by lithium catalyzed anionic polymerization followed by silicon chloride linking [4,20,21,3].

Figure 35: 5-bead quarter-twisted osculated dumbbell.

Figure 36: 4-bead quarter-twisted osculated dumbbell.

IX. REFERENCES

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