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LARGE-AMPLITUDE OSCILLATORY SHEAR FLOW LOOPS FOR LONG-CHAIN BRANCHING FROM GENERAL RIGID BEAD-ROD THEORY

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ABSTRACT

General rigid bead-rod theory [Hassager, *J Chem Phys*, **60**, 4001 (1974)] explains polymer viscoelasticity from macromolecular orientation. By means of this theory, we relate the complex viscosity of polymeric liquids to the architecture of axisymmetric branched macromolecules. In this work, we explore how adding long-chain branching to polymers affects the shapes of large-amplitude oscillatory shear flow (LAOS) loops. By *loops*, we mean plots of the alternant part of the shear stress response *versus* the cosinusoidal shear rate. When non-dimensionalized with the product of the zero-shear viscosity and the shear rate amplitude, the loop shapes depend upon the sole dimensionless architectural parameter, the *macromolecular lopsidedness* of the long-chain branched macromolecule. In this work, in this way, we compare and contrast the loop shapes of macromolecular chains that are straight, with those branched. Specifically, we explore symmetric branch multiplicity, branch functionality, branch length, branch position, branch distribution and multiple branch asymmetry. We find that adding branching collapses and distorts the loops. We then find that, so long as branch length, branch position and branch distribution are held constant, and so long as the branching is symmetric about the center of mass, the peak shear stress increases with branch multiplicity. We also find that branch functionality hardly affects the loops.

Keywords: general rigid bead-rod theory, polymer orientation, macromolecular lopsidedness, long-chain branching, branched polymers, large-amplitude oscillatory shear flow loops.

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I. INTRODUCTION

Though our work on long-chain branching is mainly curiosity-driven, its uses have not escaped our attention (see Sections 2.4.9, 4.8.2 and 7.2 of [1]). For instance, the processabilities of molten plastics are commonly improved with long-chain branching. This can be accomplished either by blending with a long-chain branching material, such as high-pressure polyethylene (see PART III, Chapter 6 of [2]; see Chapters 5 and 6 of [3]), or by adding branching to every macromolecule in the system. Either approach will raise the zero-shear viscosity, or increase the melt elasticity. Whereas the former suppresses sag (in gravity driven flows [4,5,6,7]), the latter stabilizes stretching flows as in blow molding (see Sections 10.6, 16.2, 16.3 and 16.5 of [8]), stretch blow molding (see Section 16.7 of [8]), injection molding (see Section 15.4.1 of [8]), sheet extrusion (see Section 17.5 of [8]), thermoforming or film blowing (see Section 17.1.4 of [8]; Section 3.7.6.3 of [9]).

Often, polymer processing subjects polymer melts or solutions to large and rapid deformations at crucial points in manufacturing flows. In dimensionless terms, the flows subject the polymeric liquids to large Deborah and Weissenberg numbers. In the laboratory, oscillatory shear flow subjects the polymeric liquids to a cosinusoidal shear rate, so that the Deborah and Weissenberg numbers can be adjusted separately. Previous work, has shown that whereas LAOS does not amplify subtle changes in Deborah number dependence (at low Weissenberg number), it does amplify subtle differences in Weissenberg number dependence [10,11]. In this paper, we thus focus on the effect of long-chain branching on the behavior of polymeric liquids under large and rapid deformations.

Previous work on the effect of long-chain branching on the behavior of polymeric liquids under large and rapid deformations has limited itself to one class of branched structure called pom-poms [12]. By *pom-poms*, we mean a macromolecule in which, straight chain joins two identical branch points. By *branch points*, we mean the ends of the straight chain from which q identical arms dangle (see FIG. 1. of [12]). We call such branch multiplicity *symmetric branching*. Extending reptation theory to this special class of long-chain branched macromolecules, McLeish and Larson arrived at an objective integro-differential constitutive equation (see Section II.D.3. of [12]). They then simplified this to its differential approximation (see Section V. of [12]). Hoyle *et al.* [13] and Hoyle [14] then measured the behavior of molten long-chain branched polyethylene, of otherwise unknown branching structure, in LAOS. If the number of identical dangling arms q were replaced by a discrete spectrum q_i of non-integers, the reptation constitutive equation for pom-poms could be fit to the LAOS measurements. Using Fourier analysis of the measured shear stress responses, Hoyle *et al.* [13] and Hoyle [14] found (i) that higher harmonics differ for differently branched polyethylene (see Fig. 12 of [13]) and (ii) that the limits of linear viscoelasticity in oscillatory shear flow differ for differently branched polyethylene (Fig. 13 through 15 of [13]). They also find that these limits of linear viscoelasticity are much larger than those for linear polymers ($\lambda\dot{\gamma}^0 > 1$), a finding consistent with general rigid bead-rod theory applied to long-chain backbone branched macromolecules (see Fig. 11 of [15]).

In this paper, we seek a constitutive equation that will apply to a broader range of long-chain branched architectures. We want to explore the roles of

symmetric branch multiplicity, branch functionality, branch length, branch position, branch distribution and of multiple branch asymmetry. For this we use general rigid bead-rod theory ([16,17,18 ,19,20]; **EXAMPLE 16.7-1** of [21] or **EXAMPLE 13.6-1** of [22]) bridged to continuum theory (see Section X. of [20]; [18]).

II. METHOD

In general rigid bead-rod theory, we construct our branched macromolecules from sets of beads whose positions, relative to one another, are fixed. General rigid bead-rod theory is thus not to be confused with a freely jointed chain, where the beads are rigidly separated but where the joints rotate freely (Section IV. of [19]). Our branched macromolecular bead-rod models are suspended in a Newtonian solvent. We neglect interactions of the solvent velocity fields, be they between nearest beads [23,24] or nearest macromolecules. To any such collection of bead masses, we can associate a *moment of inertia ellipsoid* (MIE) whose center is the center of mass, and whose principal moments of inertia match those of the macromolecule. The MIE thus determines the orientability of the macromolecules, and thus, the polymer contribution to the rheological properties. Our use of moment of inertia ellipsoids is not to be confused with replacing the macromolecule with an ellipsoid of revolution, with its own hydrodynamic environment [25].

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

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

so that:

$$\mathbf{R} = \frac{1}{M} \sum_{i=1}^N m_i \mathbf{r}_i \quad (2)$$

where, N is the total number of beads and $M \equiv \sum_{i=1}^N m_i$, the total mass. Since we construct our branched macromolecules with identical beads of diameter d and mass m , then $M \equiv mN$, and thus the center of mass is:

$$\mathbf{R} = \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i \quad (3)$$

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*. For our branched macromolecules $\hat{\delta}_3$ is always along the backbone. In this study, to allow us to explore all of the number of branches, branch length, branch position or branch distribution, we use a 5-bead backbone throughout.

The position vector of the i th bead with respect to the center of mass is given by (Eq. (16.7-16) of [21]; or Eq. (13.6-16) of [22]):

$$\mathbf{R}_i \equiv [R_{i1}, R_{i2}, R_{i3}] \quad (4)$$

Table 3 lists such bead positions for each of the macromolecular architectures, branched or not, studied herein. The collection of macromolecules, all sharing the same 5-bead backbone, will allow us to explore the number of branches, branch length, branch position or branch distribution.

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 [21], or (13.6-17) and (13.6-18) of [22]):

$$I_1 \equiv m \sum_{i=1}^N (R_{i2}^2 + R_{i3}^2) \quad (5)$$

$$I_2 \equiv m \sum_{i=1}^N (R_{i1}^2 + R_{i3}^2) \quad (6)$$

$$I_3 \equiv 2m \sum_{i=1}^N R_{i1}^2 \quad (7)$$

where the subscript i is the bead number. We design each structure by first rigidly connecting nearest bead centers with massless dimensionless rods. Throughout our work L is thus this center to center distance between nearest bead centers. We then complete the general rigid bead-rod construction by rigidly connecting the remaining bead centers to their nearest neighbours. In this work, L is the center to center distance between adjacent beads along the backbone, which is also the center to center distance between adjacent beads along each branch.

If the macromolecular structure is axisymmetric, so will be its moment of inertia ellipsoid. By *axisymmetric*, we mean that both the macromolecule and its moment of inertia ellipsoid, have at least one axis of symmetry. Further, if the macromolecular structure is axisymmetric, at least two of its principal moments of inertia equate, at any angle from the molecular axis, so that $I_1 = I_2$. In this work, we thus restrict our study to the axisymmetric branched structures shown in Table 4 through Table 9.

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

$$G(s) \equiv (2\eta_s + n\zeta L^2 a) \delta(s) + nkT b e^{-s/\lambda} \quad (8)$$

which nondimensionalizes as:

$$\frac{G(s)}{nkT} = \frac{\delta(s)}{kT} \left(\frac{2\eta_s}{n} + \zeta L^2 a \right) + b e^{-s/\lambda} \quad (9)$$

and in which (Eqs. (16.7-38) of [21] or Eqs. (13.6-44), (13.6-45), and (13.6-46) of [22]):

$$a \equiv \frac{2I_1 + I_3}{6mL^2} - \frac{(I_1 - I_3)^2}{5mL^2 I_1} \quad (10)$$

$$b \equiv \frac{3(I_1 - I_3)^2}{5I_1^2} \quad (11)$$

$$v \equiv \frac{6mL^2}{I_1} \quad (12)$$

The three quantities a , b and v 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.

The relaxation time can be expressed as follows:

$$\lambda \equiv \frac{\zeta I_1}{6mkT} \equiv \frac{\zeta L^2}{\nu kT} \quad (13)$$

where:

$$\zeta \equiv 3\pi d\eta_s \quad (14)$$

and, for the rigid dumbbell:

$$\lambda_0 \equiv \frac{\zeta L^2}{12kT} = \frac{\pi d\eta_s L^2}{4kT} \quad (15)$$

which nondimensionalizes as:

$$\frac{nkT\lambda_0}{\eta_s} \equiv \frac{3}{4}\phi \left(\frac{L}{d} \right)^2 \quad (16)$$

where ϕ is the bead volume fraction.

Lopsidedness, $2b/av$, is the extent to which the branched macromolecule deviates from a spherically symmetrical structure. The minimum value of $2b/av$ is 0, which is obtained 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” [20].

Dividing Eq. (13) by Eq. (15) normalizes the relaxation time of the general macromolecule to that of the simplest:

$$\frac{\lambda}{\lambda_0} \equiv \frac{12}{\nu} \quad (17)$$

We can then use Eq. (8) to calculate the polymer contribution to the stress tensor in any linear viscoelastic flow, including oscillatory shear flow, from (Eq. (1) of [19]):

$$\tau_p \equiv - \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \quad (18)$$

where all symbols are defined in Table 1 and Table 2.

III. 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:

$$\dot{\gamma}(t) = \dot{\gamma}^0 \cos \omega t \quad (19)$$

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

$$\dot{\gamma}(t) = \begin{bmatrix} 0 & \dot{\gamma}^0 \cos \omega t & 0 \\ \dot{\gamma}^0 \cos \omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (20)$$

Using the characteristic relaxation time of the branched polymeric viscoelastic fluid, λ , we can nondimensionalize Eq. (19) as:

$$\lambda \dot{\gamma}(t) = \lambda \dot{\gamma}^0 \cos \lambda \omega (t/\lambda) \quad (21)$$

where, $\lambda \omega$ and $\lambda \dot{\gamma}^0$ are the Deborah and Weissenberg numbers. By *large-amplitude*, we mean:

$$\lambda \dot{\gamma}^0 > \frac{1}{\nu \sqrt{2}} \quad (22)$$

from which we learn that the limit of linear viscoelasticity depends upon the macromolecular architecture, and thus differs from one structure to another.

IV. MOLECULARIZED CONTINUUM THEORY

Following the method of TABLES 6.2-1 and 6.2-2 of [26], or Table 1 of [27], we will next bridge our general rigid bead-rod theory to the corotational Jeffreys fluid (Eqs. 7.3-3 of [26]):

$$\tau + \lambda_1 \frac{\mathcal{D}}{\mathcal{D}t} \tau = -\eta_0 \left(\dot{\gamma} + \lambda_2 \frac{\mathcal{D}}{\mathcal{D}t} \dot{\gamma} \right) \quad (23)$$

whose shear relaxation function (Eq. 7.5-20 of [26]; cf. Eq. 7.3-4 of [26]):

$$G(s) = 2\eta_0 \frac{\lambda_2}{\lambda_1} \delta(s) + \frac{\eta_0}{\lambda_1} \left(1 - \frac{\lambda_2}{\lambda_1} \right) e^{-s/\lambda_1} \quad (24)$$

and the shear relaxation function for general rigid bead-rod theory, Eq. (8), share the same form. Comparing Eq. (24) with Eq. (8) yields the following bridging relations:

$$2\eta_0 \frac{\lambda_2}{\lambda_1} = 2\eta_s + anL^2\zeta \quad (25)$$

$$\frac{\eta_0}{\lambda_1} \left(1 - \frac{\lambda_2}{\lambda_1} \right) = nkTb \quad (26)$$

$$\lambda_1 = \lambda \quad (27)$$

Solving Eqs. (25) through (27) yields:

$$\lambda_2 = \frac{\lambda}{1 + \left(\frac{av}{2b} + \frac{\eta_s}{bnkT\lambda} \right)^{-1}} \quad (28)$$

$$\frac{\lambda_2}{\lambda} = \frac{1}{1 + \left(\frac{av}{2b} + \frac{\eta_s}{bnkT\lambda} \right)^{-1}} \quad (29)$$

where $av/2b \gg \frac{\eta_s}{bnkT\lambda}$, Eq. (29) becomes:

$$\frac{\lambda_2}{\lambda} = \frac{1}{1 + \frac{2b}{av}} \quad (30)$$

$$\eta_0 = \eta_s + bnkT\lambda \left(\frac{av}{2b} + 1 \right) \quad (31)$$

Substituting Eqs. (27), (28) and (31) into Eq. (23) bridges the general rigid bead-rod theory to the corotational Jeffreys fluid:

$$\tau + \lambda \frac{\mathcal{D}}{\mathcal{D}t} \tau = - \left[\eta_s + bnkT\lambda \left(\frac{av}{2b} + 1 \right) \right] \left(\dot{\gamma} + \frac{\lambda}{1 + \left(\frac{av}{2b} + \frac{\eta_s}{bnkT\lambda} \right)^{-1}} \frac{\mathcal{D}}{\mathcal{D}t} \dot{\gamma} \right) \quad (32)$$

which, for LAOS, gives the exact solution (Eq. (79) of [28]):

$$\begin{aligned} \mathbb{S} = e^{\frac{-\tau}{\text{De}}} \sin \left(\frac{\text{Wi}}{\text{De}} \sin \tau \right) & \left[-\frac{1}{\text{De}} I_1 + \frac{1}{1 + \frac{2b}{av}} I_3 + \frac{\text{Wi}}{\text{De}} \left(-\frac{1}{1 + \frac{2b}{av}} \right) I_5 \right] \\ & + e^{\frac{\tau}{\text{De}}} \cos \left(\frac{\text{Wi}}{\text{De}} \sin \tau \right) \left[-\frac{1}{\text{De}} I_2 + \frac{1}{1 + \frac{2b}{av}} I_4 - \frac{\text{Wi}}{\text{De}} \left(-\frac{1}{1 + \frac{2b}{av}} \right) I_6 \right] \end{aligned} \quad (33)$$

in which:

$$I_1 = \frac{4\text{De}}{\alpha} e^{\frac{\tau}{\text{De}}} \sum_{k=1}^{\infty} \left[-\frac{2\text{De}k^2 J_{2k}}{1 + 4k^2 \text{De}^2} \cos 2k\tau + \frac{k J_{2k}}{1 + 4k^2 \text{De}^2} \sin 2k\tau \right] \quad (34)$$

$$I_2 = \frac{2\text{De}}{\alpha} e^{\frac{\tau}{\text{De}}} \sum_{k=1}^{\infty} \left[\frac{(2k-1) J_{2k-1}}{1 + (2k-1)^2 \text{De}^2} \cos(2k-1)\tau + \frac{\text{De}(2k-1)^2 J_{2k-1}}{1 + (2k-1)^2 \text{De}^2} \sin(2k-1)\tau \right] \quad (35)$$

$$I_3 = \text{De} e^{\frac{\tau}{\text{De}}} J_1 + \text{De} e^{\frac{\tau}{\text{De}}} \sum_{k=1}^{\infty} \left[\frac{-J_{2k-1} + J_{2k+1}}{1 + 4k^2 \text{De}^2} \cos 2k\tau + (2\text{De}k) \frac{-J_{2k-1} + J_{2k+1}}{1 + 4k^2 \text{De}^2} \sin 2k\tau \right] \quad (36)$$

$$I_4 = \text{De} e^{\frac{\tau}{\text{De}}} \sum_{k=1}^{\infty} \left[\frac{-(2k-1)\text{De}(J_{2k-2} - J_{2k})}{1 + (2k-1)^2 \text{De}^2} \cos(2k-1)\tau + \frac{J_{2k-2} - J_{2k}}{1 + (2k-1)^2 \text{De}^2} \sin(2k-1)\tau \right] \quad (37)$$

$$I_5 = \frac{\text{De} e^{\frac{\tau}{\text{De}}} J_1}{\alpha} + \text{De} e^{\frac{\tau}{\text{De}}} \sum_{k=1}^{\infty} \left[\frac{J_{2k-2} + 2J_{2k} + J_{2k+2}}{2(1 + 4\text{De}^2 k^2)} \cos 2k\tau + (\text{De}k) \frac{J_{2k-2} + 2J_{2k} + J_{2k+2}}{1 + 4\text{De}^2 k^2} \sin 2k\tau \right] \quad (38)$$

$$I_6 = \frac{\text{De}}{2} e^{\frac{\tau}{\text{De}}} \sum_{k=1}^{\infty} \left[\frac{-\text{De}(2k-1)(J_{2k-3} + 2J_{2k-1} + J_{2k+1})}{1 + (2k-1)^2 \text{De}^2} \cos(2k-1)\tau \right. \\ \left. + \frac{J_{2k-3} + 2J_{2k-1} + J_{2k+1}}{1 + (2k-1)^2 \text{De}^2} \sin(2k-1)\tau \right] \quad (39)$$

For brevity, we just write J_m to mean $J_m(\alpha)$ where α is given by (see after Eq. (5) of [29] or before Eq. (123) of [30]):

$$\alpha \equiv \frac{\dot{\gamma}^0}{\omega} \quad (40)$$

which is the ratio of the Weissenberg $\lambda\dot{\gamma}^0$ and the Deborah $\lambda\omega$ numbers. Our main result Eq. (33) [with Eqs. (34) through (39)], is the molecularized continuum theory: the general rigid bead-rod theory bridged to the corotational Jeffreys fluid.

V. BRANCHING ARCHITECTURE AND LOOP SHAPE

We next use our main result, Eq. (33) [with Eqs. (34) through (39)], to explore the roles of symmetric branch multiplicity, branch functionality, branch length, branch position, branch distribution and of multiple branch asymmetry on the shapes of LAOS loops. By *loops*, we mean plots of the alternant part of the shear stress response *versus* the cosinusoidal shear rate [31,32,33,34,35,36]. For the loops in the upcoming Subsections V.a. through V.f., we choose $\lambda\dot{\gamma}^0 = \lambda\omega = 1$, so that the reference loop for the unbranched material is distorted from elliptical, and so that Eq. (22) is satisfied. We use our main result Eq. (33) [with Eqs. (34) through (39)] to construct Figure 1 through Figure 6.

a. SYMMETRIC BRANCH MULTIPLICITY

In this subsection, we use our main result, Eq. (33), to see how symmetric branch multiplicity affects the LAOS loops. Recall that, by *symmetric branching*, we mean that the macromolecule is symmetric about the $\hat{\delta}_1\hat{\delta}_2$ plane through the center of mass. By *branch multiplicity*, we mean the number of sets of branches. For instance, for trifunctional branching, a branch multiplicity of two, means two trifunctional branch sets. Table 4 illustrates unbranched Macromolecule 1, and backbone-branched Macromolecules 2, 3 and 4, that is, those we use for our study of symmetric branch multiplicity. Table 4 also lists our results from general rigid bead-rod theory. From Figure 1, we learn that branching increases peak shear stress and narrows the loop. Also, we learn that, from general rigid bead-rod theory, increasing branch multiplicity increases the peak shear stress.

b. BRANCH FUNCTIONALITY

Here, we use our main result, Eq. (33), to see how branch functionality affects the LAOS loops. By *branch functionality*, we mean the number of branches emanating from the same backbone-bead. Table 5 illustrates unbranched Macromolecule 1, and backbone-branched Macromolecules 2 and 5. From Figure 2, we learn that branch functionality hardly affects the shear stress response in LAOS (unless, of course, the functionality drops to zero, as for the unbranched Macromolecule 1 loop).

c. BRANCH LENGTH

In this subsection, we use our main result, Eq. (33), to see how branch length affects the LAOS loops. Table 6 illustrates backbone-branched Macromolecules 2, 6 and 7. From Figure 3, we learn that increasing the branch length, decreases the peak stress.

d. BRANCH POSITION

We next use our main result, Eq. (33), to see how branch position affects the LAOS loops. By *branch position*, we mean which place on the backbone. Table 7 illustrates backbone-branched Macromolecules 2, 8 and 9. From Figure 4, we learn that positioning the branches at the backbone end increases the peak stress.

e. BRANCH DISTRIBUTION

In this subsection, we use our main result, Eq. (33), to see how branch distribution affects the LAOS loops. By *branch distribution*, we mean spreading an q -functional branch over more than one backbone-bead, without altering the orientation of each q -functional branch. For instance, in this subsection, we distribute a trifunctional branch over 3 backbone-beads. Table 8 illustrates backbone-branched Macromolecules 2, 10, 11 and 12. From Figure 5, we learn that distributing the branches symmetrically along the backbone (Macromolecule 12), increases the peak stress.

f. MULTIPLE BRANCH ASYMMETRY

Finally, we use our main result, Eq. (33), to see how multiple branch asymmetry affects the LAOS loops. By *asymmetric branching*, we mean that the macromolecule is not symmetric about the $\hat{\delta}_1\hat{\delta}_2$ plane through the center of mass. Table 9 illustrates backbone-branched Macromolecules 3 and 13. From Figure 6, we learn that not only does branch symmetry matter, but so does the asymmetric positioning of the branching sets. Also, we learn that, from general rigid bead-rod theory, positioning multiple branch sets asymmetrically (Macromolecule 13), increases the peak stress.

VI. CONCLUSION

From Subsections V.a. and V.b., we learn from general rigid bead-rod theory, the peak shear stress in LAOS can be used as a measure of the number of branches, regardless of the branch functionality. However, from Subsections V.c. through V.f., we learn that to use the peak shear stress in LAOS effectively as a measure of the number of branches, we must hold branch length, branch position, branch distribution and multiple branch asymmetry constant. Without holding one or more of these constant, we can expect scatter when correlating peak shear stress in LAOS with the number of branches. Industrially, for a homologous series of resins, the branch length, branch position, branch distribution and multiple branch asymmetry are often constant from product to product [15]. By *homologous series*, we mean resins from the same polymerization reactor, produced with the same polymer chemistry.

Whereas work prior to this paper has focused on symmetrically branched pom-poms, with the exception of Macromolecule 15 of [20], ours has not. However, general rigid bead-rod theory can be used for asymmetrically branched pom-poms. It can also be used to explore the role of crossbar length, branch length, branch functionality (q), or even to explore pairs of differing branch functionality of pom-poms. We know of no other macromolecular theory flexible enough to address this range of branching questions (cf. Chapter 9 of

[37]). We leave this important exploration of pom-pom branching for another day.

In this work, we have relied upon a constitutive equation that is bridged to molecular theory (see Section I.). The advantage of our main result, Eq. (33), is that we can explore the role of molecular architecture without calculating the orientation distribution function. Still, it would be interesting to deepen our understanding of how branching affects the orientation dynamics in LAOS, and for this, we would follow ([16,17,18,19,20,38,39,40,41]; **EXAMPLE 16.7-1** of [21] or **EXAMPLE 13.6-1** of [22]). We have yet to explore this possibility.

In this work, although we focused on shear stress response loops in LAOS, frequency-matched response loops of the normal stress differences might be at least as interesting [42,43,44]. We leave this for another day.

Many polymer processing problems have yielded to analytical solution for the Oldroyd 8-constant model, and this model includes corotational Jeffreys as a special case. Engineers can also use the Oldroyd 8-constant framework in polymer processing, as for wire coating (mindful of the errata following Ref. 32 of [28], see Case III in [45]), and for corrugated wire coated through a corrugated die (see Section 3. of [46]; Section 2. of [47]), and for plastic pipe extrusion for elliptical pipe ([48,49]), and also for extrusion from an eccentric annular pipe die (Case II in [45];[50,51,52]). Our bridging relations, Eqs. (27) through (31), and Table 4 through Table 9, can thus be used with these analytical solutions to explore the role of branching in polymer processing.

One might prefer to add other comparisons with experiment, and specifically with relevant shear stress LAOS loops *versus* branching architecture observations. However, we know of no experimental measurements wherein symmetric branch multiplicity, branch functionality, branch length, branch position, branch distribution or multiple branch asymmetry is varied or controlled. In other words, to our knowledge, the structural details explored in this paper have yet to be explored in the laboratory.

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: Dimensional Variables.

Name	Unit	Symbol
Angular frequency	t^{-1}	ω
Bead diameter	L	d
Bead friction coefficient, [Eq. (14)]	M/t	ζ
Cartesian coordinates	L	x, y, z
Cartesian coordinates with respect to the center of mass	L	$\hat{\delta}_1, \hat{\delta}_2, \hat{\delta}_3$
Element for Kronecker delta, [Eq. (8)]	t^{-1}	$\delta(s)$
Energy values in molecular-scale systems	ML^2/t^2	kT
Extra stress tensor, [Eq. (23)]	M/Lt^2	τ
Macromolecular center of mass, [Eq. (3)]	L	$\mathbf{R}$
Mass of each bead	M	m_i
Moments of inertia, [Eqs. (5) through (7)]	ML^2	I_1, I_2, I_3
Number of dumbbells per unit volume	$1/L^3$	n
Oldroyd constant, relaxation time	t	λ_1
Oldroyd constant, retardation time	t	λ_2
Polymer contribution to the stress tensor, [Eq. (18)]	M/Lt^2	τ_p
Position vector of the i th bead and j th element with respect to the center of mass, [Eq. (4)]	L	R_{ij}
Position vector of the i th bead with respect to the center of mass, [Eq. (4)]	L	$\mathbf{R}_i$
Position vector of the i th bead, [Eq. (3)]	L	$\mathbf{r}_i$
Rate-of-strain tensor, [Eq. (23)]	t^{-1}	$\dot{\gamma}$
Relaxation time of rigid dumbbell, [Eq. (15)]	t	λ_0
Relaxation time of solution, Eq. (13)	t	λ

Shear rate amplitude, [Eq. (19)]	t^{-1}	$\dot{\gamma}^0$
Shear rate at specific time t' , [Eq. (18)]	t^{-1}	$\dot{\gamma}(t')$
Shear rate tensor, [Eq. (19)]	t^{-1}	$\dot{\boldsymbol{\gamma}}(t)$
Shear rate, [Eq. (19)]	t^{-1}	$\dot{\gamma}(t)$
Shear relaxation function, [Eq. (8)]	M/Lt^2	$G(s)$
Solvent viscosity	M/Lt	η_s
Specific time, [Eq. (18)]	t	t'
Time	t	t
Time difference	t	$s \equiv t - t'$
Total mass	M	M
Viscosity, zero shear	M/Lt	η_0

Legend: $M \equiv$ mass; $L \equiv$ length; $t \equiv$ time

Table 2: Dimensionless Variables and Groups.

Name	Symbol
Bead volume fraction [Eq. (16)]	ϕ
Bessel function of first kind, m th order, argument σ	$J_m \equiv J_m(\sigma) \equiv \sum_{k=0}^{\infty} \frac{(-1)^k}{(m+k)!k!} \left(\frac{\sigma}{2}\right)^{m+2k}$
Branch functionality	q
Constant in [Eq. (10)]	a
Constant in [Eq. (11)]	b
Constant in [Eq. (12)]	ν
Constant in Eq. (40)	$\alpha \equiv \text{Wi}/\text{De}$
Deborah number, oscillatory shear	$\text{De} \equiv \lambda\omega$
Integral-defined functions [Eqs. (34) through (39)]	$I_1, I_2, \dots, I_6$
Shear stress [Eq. (33)]	$\mathbb{S} \equiv \tau_{yx}/\eta_0\dot{\gamma}^0$
Total number of beads	N
Weissenberg number	$\text{Wi} \equiv \lambda\dot{\gamma}^0$
Time	$\tau \equiv \omega t$

Table 3: Bead positions for each macromolecule.

	Macromolecule	$L[R_{i1}, R_{i2}, R_{i3}]$
1		$[0, 0, -2]; [0, 0, -1]; [0, 0, 0]; [0, 0, 1]; [0, 0, 2].$
2		$[0, 0, -2]; [0, 0, -1]; [0, 0, 0]; [0, 0, 1]; [0, 0, 2]; [1, 0, 0]; [2, 0, 0]; [3, 0, 0]; [4, 0, 0]; [5, 0, 0];$ $\left[-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right]; \left[-\frac{1}{2}, -\frac{\sqrt{3}}{2}, 0\right]; [-1, \sqrt{3}, 0]; [-1, -\sqrt{3}, 0]; \left[-\frac{3}{2}, \frac{3\sqrt{3}}{2}, 0\right]; \left[-\frac{3}{2}, -\frac{3\sqrt{3}}{2}, 0\right];$ $[-2, 2\sqrt{3}, 0]; [-2, -2\sqrt{3}, 0]; \left[-\frac{5}{2}, \frac{5\sqrt{3}}{2}, 0\right]; \left[-\frac{5}{2}, -\frac{5\sqrt{3}}{2}, 0\right].$
3		$[0, 0, -2]; [0, 0, -1]; [0, 0, 0]; [0, 0, 1]; [0, 0, 2]; [1, 0, -1]; [2, 0, -1]; [3, 0, -1]; [4, 0, -1]; [5, 0, -1];$ $\left[-\frac{1}{2}, \frac{\sqrt{3}}{2}, -1\right]; \left[-\frac{1}{2}, -\frac{\sqrt{3}}{2}, -1\right]; [-1, \sqrt{3}, -1]; [-1, -\sqrt{3}, -1]; \left[-\frac{3}{2}, \frac{3\sqrt{3}}{2}, -1\right]; \left[-\frac{3}{2}, -\frac{3\sqrt{3}}{2}, -1\right];$ $[-2, 2\sqrt{3}, -1]; [-2, -2\sqrt{3}, -1]; \left[-\frac{5}{2}, \frac{5\sqrt{3}}{2}, -1\right]; \left[-\frac{5}{2}, -\frac{5\sqrt{3}}{2}, -1\right];$ $[1, 0, 1]; [2, 0, 1]; [3, 0, 1]; [4, 0, 1]; [5, 0, 1];$ $\left[-\frac{1}{2}, \frac{\sqrt{3}}{2}, 1\right]; \left[-\frac{1}{2}, -\frac{\sqrt{3}}{2}, 1\right]; [-1, \sqrt{3}, 1]; [-1, -\sqrt{3}, 1]; \left[-\frac{3}{2}, \frac{3\sqrt{3}}{2}, 1\right]; \left[-\frac{3}{2}, -\frac{3\sqrt{3}}{2}, 1\right];$ $[-2, 2\sqrt{3}, 1]; [-2, -2\sqrt{3}, 1]; \left[-\frac{5}{2}, \frac{5\sqrt{3}}{2}, 1\right]; \left[-\frac{5}{2}, -\frac{5\sqrt{3}}{2}, 1\right].$
4		$[0, 0, -2]; [0, 0, -1]; [0, 0, 0]; [0, 0, 1]; [0, 0, 2]; [1, 0, -2]; [2, 0, -2]; [3, 0, -2]; [4, 0, -2]; [5, 0, -2];$ $\left[-\frac{1}{2}, \frac{\sqrt{3}}{2}, -2\right]; \left[-\frac{1}{2}, -\frac{\sqrt{3}}{2}, -2\right]; [-1, \sqrt{3}, -2]; [-1, -\sqrt{3}, -2]; \left[-\frac{3}{2}, \frac{3\sqrt{3}}{2}, -2\right];$ $\left[-\frac{3}{2}, -\frac{3\sqrt{3}}{2}, -2\right]; [-2, 2\sqrt{3}, -2]; [-2, -2\sqrt{3}, -2]; \left[-\frac{5}{2}, \frac{5\sqrt{3}}{2}, -2\right]; \left[-\frac{5}{2}, -\frac{5\sqrt{3}}{2}, -2\right];$ $[1, 0, 0]; [2, 0, 0]; [3, 0, 0]; [4, 0, 0]; [5, 0, 0];$ $\left[-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right]; \left[-\frac{1}{2}, -\frac{\sqrt{3}}{2}, 0\right]; [-1, \sqrt{3}, 0]; [-1, -\sqrt{3}, 0]; \left[-\frac{3}{2}, \frac{3\sqrt{3}}{2}, 0\right];$ $\left[-\frac{3}{2}, -\frac{3\sqrt{3}}{2}, 0\right]; [-2, 2\sqrt{3}, 0]; [-2, -2\sqrt{3}, 0]; \left[-\frac{5}{2}, \frac{5\sqrt{3}}{2}, 0\right]; \left[-\frac{5}{2}, -\frac{5\sqrt{3}}{2}, 0\right];$ $[1, 0, 2]; [2, 0, 2]; [3, 0, 2]; [4, 0, 2]; [5, 0, 2];$ $\left[-\frac{1}{2}, \frac{\sqrt{3}}{2}, 2\right]; \left[-\frac{1}{2}, -\frac{\sqrt{3}}{2}, 2\right]; [-1, \sqrt{3}, 2]; [-1, -\sqrt{3}, 2]; \left[-\frac{3}{2}, \frac{3\sqrt{3}}{2}, 2\right];$ $\left[-\frac{3}{2}, -\frac{3\sqrt{3}}{2}, 2\right]; [-2, 2\sqrt{3}, 2]; [-2, -2\sqrt{3}, 2]; \left[-\frac{5}{2}, \frac{5\sqrt{3}}{2}, 2\right]; \left[-\frac{5}{2}, -\frac{5\sqrt{3}}{2}, 2\right].$

5		$[0,0,-2];[0,0,-1];[0,0,1];[0,0,2];[0,0,0];[1,0,0];[2,0,0];[3,0,0];[4,0,0];[5,0,0];$ $[-1,0,0];[-2,0,0];[-3,0,0];[-4,0,0];[-5,0,0];[0,1,0];[0,2,0];[0,3,0];[0,4,0];$ $[0,5,0];[0,-1,0];[0,-2,0];[0,-3,0];[0,-4,0];[0,-5,0].$
6		$[0,0,-2];[0,0,-1];[0,0,0];[0,0,1];[0,0,2];[1,0,0];[2,0,0];[3,0,0];[4,0,0];[5,0,0];[6,0,0];$ $\left[-\frac{1}{2},\frac{\sqrt{3}}{2},0\right];\left[-\frac{1}{2},-\frac{\sqrt{3}}{2},0\right];[-1,\sqrt{3},0];[-1,-\sqrt{3},0];\left[-\frac{3}{2},\frac{3\sqrt{3}}{2},0\right];\left[-\frac{3}{2},-\frac{3\sqrt{3}}{2},0\right];$ $[-2,2\sqrt{3},0];[-2,-2\sqrt{3},0];\left[-\frac{5}{2},\frac{5\sqrt{3}}{2},0\right];\left[-\frac{5}{2},-\frac{5\sqrt{3}}{2},0\right];[-3,3\sqrt{3},0];[-3,-3\sqrt{3},0].$
7		$[0,0,-2];[0,0,-1];[0,0,0];[0,0,1];[0,0,2];[1,0,0];[2,0,0];[3,0,0];[4,0,0];[5,0,0];[6,0,0];$ $[7,0,0];\left[-\frac{1}{2},\frac{\sqrt{3}}{2},0\right];\left[-\frac{1}{2},-\frac{\sqrt{3}}{2},0\right];[-1,\sqrt{3},0];[-1,-\sqrt{3},0];\left[-\frac{3}{2},\frac{3\sqrt{3}}{2},0\right];$ $\left[-\frac{3}{2},-\frac{3\sqrt{3}}{2},0\right];[-2,2\sqrt{3},0];[-2,-2\sqrt{3},0];\left[-\frac{5}{2},\frac{5\sqrt{3}}{2},0\right];\left[-\frac{5}{2},-\frac{5\sqrt{3}}{2},0\right];$ $[-3,3\sqrt{3},0];[-3,-3\sqrt{3},0];\left[-\frac{7}{2},\frac{7\sqrt{3}}{2},0\right];\left[-\frac{7}{2},-\frac{7\sqrt{3}}{2},0\right].$
8		$[0,0,-2];[0,0,-1];[0,0,0];[0,0,1];[0,0,2];[1,0,-1];[2,0,-1];[3,0,-1];[4,0,-1];[5,0,-1];$ $\left[-\frac{1}{2},\frac{\sqrt{3}}{2},-1\right];\left[-\frac{1}{2},-\frac{\sqrt{3}}{2},-1\right];[-1,\sqrt{3},-1];[-1,-\sqrt{3},-1];\left[-\frac{3}{2},\frac{3\sqrt{3}}{2},-1\right];\left[-\frac{3}{2},-\frac{3\sqrt{3}}{2},-1\right];$ $[-2,2\sqrt{3},-1];[-2,-2\sqrt{3},-1];\left[-\frac{5}{2},\frac{5\sqrt{3}}{2},-1\right];\left[-\frac{5}{2},-\frac{5\sqrt{3}}{2},-1\right].$

9		$[0,0,-2];[0,0,-1];[0,0,0];[0,0,1];[0,0,2];[1,0,-2];[2,0,-2];[3,0,-2];[4,0,-2];[5,0,-2];$ $\left[-\frac{1}{2},\frac{\sqrt{3}}{2},-2\right];\left[-\frac{1}{2},-\frac{\sqrt{3}}{2},-2\right];[-1,\sqrt{3},-2];[-1,-\sqrt{3},-2];\left[-\frac{3}{2},\frac{3\sqrt{3}}{2},-2\right];$ $\left[-\frac{3}{2},-\frac{3\sqrt{3}}{2},-2\right];[-2,2\sqrt{3},-2];[-2,-2\sqrt{3},-2];\left[-\frac{5}{2},\frac{5\sqrt{3}}{2},-2\right];\left[-\frac{5}{2},-\frac{5\sqrt{3}}{2},-2\right].$
10		$[0,0,-2];[0,0,-1];[0,0,0];[0,0,1];[0,0,2];[1,0,0];[2,0,0];[3,0,0];[4,0,0];[5,0,0];$ $\left[-\frac{1}{2},\frac{\sqrt{3}}{2},1\right];\left[-\frac{1}{2},-\frac{\sqrt{3}}{2},1\right];[-1,\sqrt{3},1];[-1,-\sqrt{3},1];\left[-\frac{3}{2},\frac{3\sqrt{3}}{2},1\right];\left[-\frac{3}{2},-\frac{3\sqrt{3}}{2},1\right];$ $[-2,2\sqrt{3},1];[-2,-2\sqrt{3},1];\left[-\frac{5}{2},\frac{5\sqrt{3}}{2},1\right];\left[-\frac{5}{2},-\frac{5\sqrt{3}}{2},1\right].$
11		$[0,0,-2];[0,0,-1];[0,0,0];[0,0,1];[0,0,2];[1,0,-1];[2,0,-1];[3,0,-1];[4,0,-1];[5,0,-1];$ $\left[-\frac{1}{2},\frac{\sqrt{3}}{2},0\right];\left[-\frac{1}{2},-\frac{\sqrt{3}}{2},-2\right];[-1,\sqrt{3},0];[-1,-\sqrt{3},-2];\left[-\frac{3}{2},\frac{3\sqrt{3}}{2},0\right];$ $\left[-\frac{3}{2},-\frac{3\sqrt{3}}{2},-2\right];[-2,2\sqrt{3},0];[-2,-2\sqrt{3},-2];\left[-\frac{5}{2},\frac{5\sqrt{3}}{2},0\right];\left[-\frac{5}{2},-\frac{5\sqrt{3}}{2},-2\right].$
12		$[0,0,-2];[0,0,-1];[0,0,0];[0,0,1];[0,0,2];[1,0,0];[2,0,0];[3,0,0];[4,0,0];[5,0,0];$ $\left[-\frac{1}{2},\frac{\sqrt{3}}{2},2\right];\left[-\frac{1}{2},-\frac{\sqrt{3}}{2},-2\right];[-1,\sqrt{3},2];[-1,-\sqrt{3},-2];\left[-\frac{3}{2},\frac{3\sqrt{3}}{2},2\right];$ $\left[-\frac{3}{2},-\frac{3\sqrt{3}}{2},-2\right];[-2,2\sqrt{3},2];[-2,-2\sqrt{3},-2];\left[-\frac{5}{2},\frac{5\sqrt{3}}{2},2\right];\left[-\frac{5}{2},-\frac{5\sqrt{3}}{2},-2\right].$

13		$ \begin{aligned} &[0,0,-2];[0,0,-1];[0,0,0];[0,0,1];[0,0,2];[1,0,-2];[2,0,-2];[3,0,-2];[4,0,-2];[5,0,-2]; \\ &\left[-\frac{1}{2},\frac{\sqrt{3}}{2},-2\right];\left[-\frac{1}{2},-\frac{\sqrt{3}}{2},-2\right];[-1,\sqrt{3},-2];[-1,-\sqrt{3},-2];\left[-\frac{3}{2},\frac{3\sqrt{3}}{2},-2\right]; \\ &\left[-\frac{3}{2},-\frac{3\sqrt{3}}{2},-2\right];[-2,2\sqrt{3},-2];[-2,-2\sqrt{3},-2];\left[-\frac{5}{2},\frac{5\sqrt{3}}{2},-2\right];\left[-\frac{5}{2},-\frac{5\sqrt{3}}{2},-2\right]; \\ &[1,0,0];[2,0,0];[3,0,0];[4,0,0];[5,0,0]; \\ &\left[-\frac{1}{2},\frac{\sqrt{3}}{2},0\right];\left[-\frac{1}{2},-\frac{\sqrt{3}}{2},0\right];[-1,\sqrt{3},0];[-1,-\sqrt{3},0];\left[-\frac{3}{2},\frac{3\sqrt{3}}{2},0\right]; \\ &\left[-\frac{3}{2},-\frac{3\sqrt{3}}{2},0\right];[-2,2\sqrt{3},0];[-2,-2\sqrt{3},0];\left[-\frac{5}{2},\frac{5\sqrt{3}}{2},0\right];\left[-\frac{5}{2},-\frac{5\sqrt{3}}{2},0\right]. \end{aligned} $
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Table 4: Effect of symmetric branch multiplicity.

	Macromolecule	$\frac{I_1}{mL^2} \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
1		10	0	$\frac{4}{3}$	$\frac{3}{5}$	$\frac{3}{5}$	$\frac{3}{2}$	20
2		$\frac{185}{2}$	165	$\frac{10427}{222}$	$\frac{2523}{6845}$	$\frac{12}{185}$	$\frac{2523}{10427}$	185
3		205	330	$\frac{13295}{123}$	$\frac{375}{1681}$	$\frac{6}{205}$	$\frac{375}{2659}$	410
4		$\frac{755}{2}$	495	$\frac{182123}{906}$	$\frac{6627}{1114005}$	$\frac{12}{755}$	$\frac{6627}{182123}$	755

Table 5: Effect of branch functionality.

	Macromolecule	$\frac{I_1}{mL^2}, \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
1		10	0	$\frac{4}{3}$	$\frac{3}{5}$	$\frac{3}{5}$	$\frac{3}{2}$	20
2		$\frac{185}{2}$	165	$\frac{10427}{222}$	$\frac{2523}{6845}$	$\frac{12}{185}$	$\frac{2523}{10427}$	185
5		120	220	60	$\frac{5}{12}$	$\frac{1}{20}$	$\frac{5}{18}$	240

Table 6: Effect of branch length.

	Macromolecule	$\frac{I_1}{mL^2} \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
2		$\frac{185}{2}$	165	$\frac{10427}{222}$	$\frac{2523}{6845}$	$\frac{12}{185}$	$\frac{2523}{10427}$	185
6		$\frac{293}{2}$	273	$\frac{637163}{8790}$	$\frac{192027}{429245}$	$\frac{12}{293}$	$\frac{12968}{43029}$	293
7		220	420	$\frac{3530}{33}$	$\frac{60}{121}$	$\frac{3}{110}$	$\frac{120}{353}$	440

Table 7: Effect of branch position.

	Macromolecule	$\frac{I_1}{mL^2} \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
2		$\frac{185}{2}$	165	$\frac{10427}{222}$	$\frac{2523}{6845}$	$\frac{12}{185}$	$\frac{2523}{10427}$	185
8		$\frac{215}{2}$	165	$\frac{14753}{258}$	$\frac{1587}{9245}$	$\frac{12}{215}$	$\frac{1587}{14753}$	215
9		$\frac{297}{2}$	165	$\frac{2299}{30}$	$\frac{1}{135}$	$\frac{4}{99}$	$\frac{1}{209}$	297

Table 8: Effect of branch distribution.

	Macromolecule	$\frac{I_1}{mL^2} \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
2		$\frac{185}{2}$	165	$\frac{10427}{222}$	$\frac{2523}{6845}$	$\frac{12}{185}$	$\frac{2523}{10427}$	185
10		$\frac{205}{2}$	165	$\frac{13295}{249}$	$\frac{375}{1681}$	$\frac{12}{205}$	$\frac{375}{2659}$	205
11		$\frac{235}{2}$	165	$\frac{17717}{282}$	$\frac{1083}{11045}$	$\frac{12}{235}$	$\frac{1083}{17717}$	235
12		$\frac{265}{2}$	165	$\frac{22283}{318}$	$\frac{507}{14045}$	$\frac{12}{265}$	$\frac{507}{22283}$	265

Table 9: Effect of multiple branch asymmetry.

	Macromolecule	$\frac{I_1}{mL^2} \quad \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
3		205	330	$\frac{13295}{123}$	$\frac{375}{1681}$	$\frac{6}{205}$	$\frac{375}{2659}$	410
13		235	330	$\frac{17717}{141}$	$\frac{1083}{11045}$	$\frac{6}{235}$	$\frac{1083}{17717}$	470

Figure 1: Effect of symmetric branch multiplicity on loop shape in LAOS. *Minus* dimensionless shear stress *versus* dimensionless shear rate from Eq. (33) with $Wi = 1$ and $De = 1$. Unbranched Macromolecule 1 (**black**, $2b/av =$) *versus* backbone-branched Macromolecules 2 (**blue**, $2b/av = 2523/10427$, trifunctional), 3 (**red**, $2b/av = 375/2659$, ditrifunctional) and 4 (**magenta**, $2b/av = 6627/182123$, tertrifunctional).

Figure 2: Effect of number of branches on loop shape in LAOS. *Minus* dimensionless shear stress *versus* dimensionless shear rate from Eq. (33) with $Wi = 1$ and $De = 1$. Unbranched Macromolecule 1 (**black**, $2b/av = 3/2$), *versus* backbone-branched Macromolecules 2 (**blue**, $2b/av = 2523/10427$, trifunctional) and 5 (**red**, $2b/av = 5/18$, quadrafunctional).

Figure 3: Effect of branch length on loop shape in LAOS. *Minus* dimensionless shear stress *versus* dimensionless shear rate from Eq. (33) with $Wi = 1$ and $De = 1$. Trifunctionally backbone-branched Macromolecules 2 (**blue**, $2b/av = 2523/10427$, 5-bead branch), 6 (**red**, $2b/av = 12968/43029$, 6-bead branch) and 7 (**black**, $2b/av = 120/353$, 7-bead branch).

Figure 4: Effect of branch position on loop shape in LAOS. *Minus* dimensionless shear stress *versus* dimensionless shear rate from Eq. (33) with $Wi = 1$ and $De = 1$. Trifunctionally backbone-branched Macromolecules 2 (**blue**, $2b/av = 2523/10427$, backbone center), 8 (**red**, $2b/av = 1587/14753$, between backbone center and end) and 9 (**black**, $2b/av = 1/209$, backbone end).

Figure 5: Effect of branch distribution on loop shape in LAOS. *Minus* dimensionless shear stress *versus* dimensionless shear rate from Eq. (33) with $Wi = 1$ and $De = 1$. Trifunctionally backbone-branched Macromolecules 2 (**blue**, $2b/av = 2523/10427$, undistributed, backbone-centered), 10 (**red**, $2b/av = 375/2659$, distributed symmetrically over beads 2, 3 and 4), 11 (**black**, $2b/av = 1083/17717$, distributed asymmetrically over beads 1, 2 and 3), 12 (**magenta**, $2b/av = 507/22283$, distributed symmetrically over beads 1, 3 and 5).

Figure 6: Effect of multiple branch symmetry on loop shape in LAOS. *Minus* dimensionless shear stress *versus* dimensionless shear rate from Eq. (33) with $Wi = 1$ and $De = 1$. Ditrifunctionally backbone-branched Macromolecules 3 (**red**, $2b/av = 375/2659$, beads 2 and 4), 13 (**blue**, $2b/av = 1083/17717$, beads 1 and 3).

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