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COLE-COLE RELATION FOR LONG-CHAIN BRANCHING FROM GENERAL RIGID BEAD-ROD THEORY

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ABSTRACT

Empirically, we find that parametric plots of the imaginary *versus* real parts of the complex viscosity may depend neither on temperature, nor on average molecular weight. Moreover, for fixed polydispersity, these Cole-Cole curves amplify both rightward and upward with long-chain branching content. In this paper, we find that general rigid bead-rod theory [O. Hassager, "Kinetic theory and rheology of bead-rod models for macromolecular solutions. II. Linear unsteady flow properties," *J. Chem. Phys.* **60**(10), 4001–4008 (1974)] can explain these rightward and upward amplifications. We explore the effects of branching along a straight chain in small-amplitude oscillatory shear flow. Specifically, we explore the number of branches, branch length, branch position and branch distribution.

Keywords: Cole-Cole plot, general rigid bead-rod theory, polymer orientation, complex viscosity, zero-shear viscosity, limits of linear viscoelasticity, branched polymers.

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I. INTRODUCTION

Into rheology, Cole and Cole (1941) introduced plots of the in-phase *versus* out-of-phase parts of complex permittivity (Subsection III.A. of [1]) and complex viscosity (Subsections VI.D. and VI.E. of [1]). Empirically, parametric plots of the imaginary *versus* real parts of the complex viscosity (or complex modulus) may depend neither on temperature (see Figure 3 of [2]), nor on average molecular weight (Figure 3 of [2]). Moreover, for fixed polydispersity (Figure 3 of [2]), the Cole-Cole viscosity curves amplify both rightward and upward with long-chain branching content. In this paper, we find that general rigid bead-rod theory [3] can explain these rightward and upward amplifications. We explore the effects of branching along a straight chain in small-amplitude oscillatory shear flow. Specifically, in Subsections V.b. through V.e., we explore the number of branches, branch length, branch position and branch distribution. Though our work here is mainly motivated by curiosity, the many applications for this work have not escaped our attention. We will explore these applications in the Worked Example proceeding the Conclusion. For our symbols, dimensional and non-dimensional, respectively listed in Table 1 and Table 2, we follow those of the corresponding textbook treatments, **EXAMPLE 16.7-1** of [4] (or **EXAMPLE 13.6-1** of [5]).

II. METHOD

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

$$G(s) \equiv (2\eta_s + n\zeta L^2 a) \delta(s) + nkTbe^{-s/\lambda} \quad (1)$$

which nondimensionalizes as:

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

and in which (Eqs. (16.7-38) of [6] or Eqs. (13.6-44), (13.6-45), and (13.6-46) of [7]:

$$a \equiv \frac{2I_1 + I_3}{6mL^2} - \frac{(I_1 - I_3)^2}{5mL^2 I_1} \quad (3)$$

$$b \equiv \frac{3(I_1 - I_3)^2}{5I_1^2} \quad (4)$$

$$\nu \equiv \frac{6mL^2}{I_1} \quad (5)$$

where (first paragraph of Section VI.b, above Eq. (44) of [8]):

$$0 \leq b \leq \frac{3}{5} \quad (6)$$

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.

The relaxation time can be expressed as follows:

$$\lambda \equiv \frac{\zeta I_1}{6mkT} \equiv \frac{\zeta L^2}{\nu kT} \quad (7)$$

where:

$$\zeta \equiv 3\pi d\eta_s \quad (8)$$

and, for the rigid dumbbell:

$$\lambda_0 \equiv \frac{\zeta L^2}{12kT} = \frac{\pi d\eta_s L^2}{4kT} \quad (9)$$

which nondimensionalizes as:

$$\frac{nkT\lambda_0}{\eta_s} \equiv \frac{3}{4}\varphi\left(\frac{L}{d}\right)^2 \quad (10)$$

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” [9].

Dividing Eq. (7) by Eq. (9) normalizes the relaxation time of the general macromolecule to that of the simplest:

$$\frac{\lambda}{\lambda_0} \equiv \frac{12}{v} \quad (11)$$

We can then use Eq. (1) to calculate the polymer contribution to the stress tensor in any linear viscoelastic flow, including oscillatory shear flow, from (Eq. (1) of [10]).

$$\tau_p \equiv -\int_{-\infty}^t G(t-t')\dot{\gamma}(t')dt' \quad (12)$$

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:

$$\dot{\gamma}(t) = \dot{\gamma}^0 \cos \omega t \quad (13)$$

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

$$\dot{\gamma}(t) = \begin{bmatrix} 0 & \dot{\gamma}^0 \cos \omega t & 0 \\ \dot{\gamma}^0 \cos \omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (14)$$

Using the characteristic relaxation time of the branched polymeric viscoelastic fluid, λ , we can nondimensionalize Eq. (13) as:

$$\lambda \dot{\gamma}(t) = \lambda \dot{\gamma}^0 \cos \lambda \omega (t/\lambda) \quad (15)$$

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:

$$\lambda \dot{\gamma}^0 \ll \frac{1}{v\sqrt{2}} \quad (16)$$

whose left side is the macromolecular Weissenberg number. From Eq. (16), we learn that branched structures with higher v 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. (16) is satisfied, the shear stress response is sinusoidal:

$$\begin{aligned} \tau_{21} &= -\dot{\gamma}^0 (\eta'(\omega) \cos \omega t + \eta''(\omega) \sin \omega t) \\ &= \frac{-\dot{\gamma}^0}{\omega} (G''(\omega) \cos \omega t + G'(\omega) \sin \omega t) \end{aligned} \quad (17)$$

with parts in-phase and out-of-phase with the shear rate, and the more complicated first normal stress difference responses:

$$\tau_{11} - \tau_{22} = -(\dot{\gamma}^0)^2 (\Psi_1^d(\omega) + \Psi_1'(\omega) \cos \omega t + \Psi_1''(\omega) \sin \omega t) \quad (18)$$

$$\tau_{22} - \tau_{33} = +(\dot{\gamma}^0)^2 (\Psi_2^d(\omega) + \Psi_2'(\omega) \cos \omega t + \Psi_2''(\omega) \sin \omega t) \quad (19)$$

which we will return to in the Conclusion.

In this paper, we follow the Gemant convention [11,12,13]:

$$\eta^* \equiv \eta' - i\eta'' \quad (20)$$

$$\Psi_1^* \equiv \Psi_1' - i\Psi_1'' \quad (21)$$

$$\Psi_2^* \equiv \Psi_2' - i\Psi_2'' \quad (22)$$

Substituting Eq. (11) into Eq. (33) of [9] and [14], for general rigid bead-rod theory, for the polymer contribution to the real part of the complex viscosity we get:

$$\frac{(\eta' - \eta_s)}{nkT\lambda_0} = 6a \left\{ 1 + \frac{2b}{av} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (23)$$

and for *minus* the imaginary part (Eq. (34) of [9]):

$$\frac{\eta''}{nkT\lambda_0} = 6a \left\{ \frac{2b}{av} \frac{\lambda\omega}{1 + (\lambda\omega)^2} \right\} \quad (24)$$

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. (2) is the source of the fluid elasticity. From Eq. (23) and (24) both η' and η'' are amplified by the same factor $1/nkT\lambda_0$.

Eqs. (23) and (24) are subject to inequalities Eq. (6) for b , and (below **TABLE 16.7-1** of [15]):

$$0 \leq \frac{2b}{av} \leq \frac{3}{2} \quad (25)$$

for the macromolecular lopsidedness.

As $\lambda\omega \rightarrow 0$, Eqs. (23) and (24) give:

$$\frac{(\eta_0 - \eta_s)}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow 0} \frac{(\eta' - \eta_s)}{nkT\lambda_0} = 6a \left\{ 1 + \frac{2b}{av} \right\} \quad (26)$$

$$\frac{\eta_0''}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow 0} \frac{\eta''}{nkT\lambda_0} = 0 \quad (27)$$

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

$$\frac{(\eta_\infty' - \eta_s')}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow \infty} \frac{(\eta' - \eta_s')}{nkT\lambda_0} = 6a \quad (28)$$

$$\frac{\eta_\infty''}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow \infty} \frac{\eta''}{nkT\lambda_0} = 0 \quad (29)$$

where limits, Eqs. (26) and (28), are of course subject to Eqs. (6) and (25).

Solving Eq. (23) for the real part of the complex viscosity, we get:

$$\frac{\eta'}{nkT\lambda_0} = 6a \left\{ 1 + \frac{2b}{av} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} + \frac{\eta_s}{nkT\lambda_0} \quad (30)$$

and if:

$$\frac{\eta_s}{nkT\lambda_0} \ll 1 \quad (31)$$

then solvent viscosity does not matter. Since the left side of Eq. (31) 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. (31) obtains, we get:

$$\frac{\eta'}{nkT\lambda_0} = 6a \left\{ 1 + \frac{2b}{av} \left(\frac{1}{1 + (\lambda\omega)^2} \right) \right\} \quad (32)$$

which we will use presently.

IV. COLE-COLE RELATIONS

Cole and Cole suggested that the complex viscosity might behave like complex permittivity, and specifically, that its frequency dependence might follow Eq. (5) of Section D. of [1] [(see also Section 3.15 of [16]):

$$\frac{\eta^* - \eta_\infty'}{\eta_0 - \eta_\infty'} = \frac{1}{1 + (i\lambda\omega)^{1-\alpha}} \quad (33)$$

$$\frac{\eta' - \eta_\infty'}{\eta_0 - \eta_\infty'} = \Re \left(\frac{1}{1 + (i\lambda\omega)^{1-\alpha}} \right) = \frac{1}{1 + (\lambda\omega)^{2(1-\alpha)} \sin^2 \left(\frac{\pi}{2}(1-\alpha) \right)} \quad (34)$$

and:

$$\frac{\eta''}{\eta_0 - \eta_\infty'} = -\Im \left(\frac{1}{1 + (i\lambda\omega)^{1-\alpha}} \right) = \frac{(\lambda\omega)^{1-\alpha} \sin \left(\frac{\pi}{2}(1-\alpha) \right)}{1 + (\lambda\omega)^{2(1-\alpha)} \sin^2 \left(\frac{\pi}{2}(1-\alpha) \right)} \quad (35)$$

and, for the special case of $\alpha = 0$:

$$\frac{\eta^* - \eta_\infty'}{\eta_0 - \eta_\infty'} = \frac{1}{1 + i\lambda\omega} \quad (36)$$

so that:

$$\frac{\eta' - \eta'_\infty}{\eta_0 - \eta'_\infty} = \Re\left(\frac{1}{1 + i\lambda\omega}\right) = \frac{1}{1 + (\lambda\omega)^2} \quad (37)$$

and:

$$\frac{\eta''}{\eta_0 - \eta'_\infty} = -\Im\left(\frac{1}{1 + i\lambda\omega}\right) = \frac{\lambda\omega}{1 + (\lambda\omega)^2} \quad (38)$$

We next rewrite Eqs. (23) and (24) as:

$$\frac{\eta' - (\eta_s + 6ankT\lambda_0)}{[\eta_s + 6ankT\lambda_0(1 + 2b/av)] - (\eta_s + 6ankT\lambda_0)} = \frac{1}{1 + (\lambda\omega)^2} \quad (39)$$

$$\frac{\eta''}{[\eta_s + 6ankT\lambda_0(1 + 2b/av)] - (\eta_s + 6ankT\lambda_0)} = \frac{\lambda\omega}{1 + (\lambda\omega)^2} \quad (40)$$

from which we learn that Eqs. (23) and (24) of the general rigid bead-rod theory, and Eqs. (36) and (37) of the Cole-Cole analogy with permittivity, share the same form.

We next derive the Cole-Cole parametric relations. Solving Eq. (32):

$$\lambda\omega = \sqrt{\frac{2b}{av} \left[\frac{1}{6a} \frac{\eta'}{nkT\lambda_0} - 1 \right]^{-1} - 1} \quad (41)$$

Substituting this into Eq. (24):

$$\frac{\eta''}{nkT\lambda_0} = \left(\frac{\eta'}{nkT\lambda_0} - 6a \right) \sqrt{\frac{2b}{av} \left[\frac{1}{6a} \frac{\eta'}{nkT\lambda_0} - 1 \right]^{-1} - 1} \quad (42)$$

which is subject to:

$$\frac{2b}{av} \left[\frac{1}{6a} \frac{\eta'}{nkT\lambda_0} - 1 \right]^{-1} \geq 1 \quad (43)$$

Eqs. (42) and (43) are subject to Eq. (25). From Eq. (42) we learn that what happens to a Cole-Cole plot when branches are introduced to macromolecular architectures depends on exactly two things: a and $2b/av$. The latter is bounded by Eq. (25), and the former is positive and otherwise unbounded.

We call Eq. (42) the *Cole-Cole relation for long-chain branching* and we nondimensionalize it as:

$$H'' = (H' - 6a) \sqrt{\frac{12b}{v} \frac{1}{H' - 6a} - 1} \quad (44)$$

which is subject to:

$$\frac{12b}{v} \frac{1}{H' - 6a} \geq 1 \quad (45)$$

and wherein:

$$H' \equiv \frac{\eta'}{nkT\lambda_0} \quad (46)$$

$$H'' \equiv \frac{\eta''}{nkT\lambda_0} \quad (47)$$

so that Eqs. (26) through (29) become:

$$H'_0 \equiv \frac{\eta_0}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow 0} H' = 6a + \frac{12b}{v} \quad (48)$$

$$H''_0 \equiv \frac{\eta''_0}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow 0} H'' = 0 \quad (49)$$

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

$$H'_\infty \equiv \frac{\eta'_\infty}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow \infty} H' = 6a \quad (50)$$

$$H''_\infty \equiv \frac{\eta''_\infty}{nkT\lambda_0} \equiv \lim_{\lambda\omega \rightarrow \infty} H'' = 0 \quad (51)$$

Since a increases with the number of branches (for both prolate (**TABLE VIII.** of [9]) and oblate (**TABLE IV.** of [8]) branching, we find that general bead-rod theory indeed explains the rightward and upward amplifications observed in Cole-Cole plots. We call Eq. (42) the *Cole-Cole relation for long-chain branching*, and Eq. (44), its dimensionless form. *Figure 1* illustrates the effect of macromolecular lopsidedness, $2b/av$, on the shapes of Cole-Cole plots.

Eq. (44) gives imaginary ordinate intercept:

$$H''(0) = i6a\sqrt{\frac{2b}{av}} + 1 \quad (52)$$

and two abscissa intercepts:

$$H'_0(0) = 6a \quad (53)$$

$$H'_\infty(0) = \frac{2b}{av} + 6a \quad (54)$$

We can rewrite Eq. (44) as:

$$H''^2 - 2\left(6\left(a + \frac{b}{v}\right)H'\right) + H'^2 = \left(\frac{6b}{v}\right)^2 \quad (55)$$

which has the general form of a circle (displaced by x_c along the abscissa):

$$y^2 + (x - x_c)^2 = R^2 \quad (56)$$

with displacement:

$$x_c = 6\left(a + \frac{b}{v}\right) \quad (57)$$

and radius:

$$R = \frac{6b}{v} \quad (58)$$

from which we learn that the dimensionless Cole-Cole plot, from general rigid bead-rod theory, is circular.

The *Cole-Cole circle* radius is then just the peak value of *minus* the dimensionless imaginary part of the complex viscosity:

$$R \equiv H_p'' \equiv \frac{\eta_p''}{nkT\lambda_0} = \frac{6b}{v} \quad (59)$$

and this *Cole-Cole circle* is centered on the abscissa at the dimensionless real part:

$$H_p' \equiv \frac{\eta_p'}{nkT\lambda_0} = 6 \left(a + \frac{b}{v} \right) \quad (60)$$

The left abscissa intercept, $x_c - R$, then matches Eq. (50), and the right abscissa intercept $x_c + R$ matches Eq. (48), as these must.

Measured values of the real part of the complex viscosity at high frequency are normally orders of magnitude below the zero shear viscosity:

$$\frac{\eta_\infty'}{\eta_0} \ll 1 \quad (61)$$

We can thus force our dimensionless Cole-Cole plot through the origin by plotting $H' - H_\infty'$ on the abscissa. From Eq. (50):

$$\frac{\eta''}{nkT\lambda_0} = \left(\frac{\eta' - \eta_\infty'}{nkT\lambda_0} \right) \sqrt{12 \frac{b}{v} \left[\frac{\eta' - \eta_\infty'}{nkT\lambda_0} \right]^{-1} - 1} \quad (62)$$

from which we learn that, from general rigid bead-rod theory, the height and width of the Cole-Cole plot depends on just one feature of the macromolecular architecture:

$$0 \leq \frac{b}{v} \leq \infty \quad (63)$$

whose numerator and denominator are subject respectively to Eq. (6) and:

$$0 \leq v \leq 12 \quad (64)$$

where for the rigid dumbbell, $v = 12$.

Eq. (62) has the general form of a circle (displaced by x_c along the abscissa):

$$\left(\frac{\eta''}{nkT\lambda_0} \right)^2 - \left(2 \left(6 \frac{b}{v} + \frac{\eta_\infty'}{nkT\lambda_0} \right) \right) \frac{\eta'}{nkT\lambda_0} + \left(\frac{\eta'}{nkT\lambda_0} \right)^2 = \frac{-\eta_\infty'}{nkT\lambda_0} \left(12 \frac{b}{v} + \frac{\eta_\infty'}{nkT\lambda_0} \right) \quad (65)$$

which has the general form:

$$y^2 - 2x_c x + x^2 = R^2 - x_c^2 \quad (66)$$

with displacement:

$$x_c = 6 \frac{b}{v} + \frac{\eta_\infty'}{nkT\lambda_0} \quad (67)$$

and radius:

$$R = 6 \frac{b}{v} \quad (68)$$

from which we learn that R is proportional to b/v , and *Figure 1* illustrates this.

Otherwise put, Eq. (68) teaches that b/v , and b/v alone, governs whether a branched macromolecule's Cole-Cole plot falls above or below its unbranched counterpart's.

Thus, if b/v of the branched macromolecule exceeds that of its unbranched counterpart, the Cole-Cole plot of the branched macromolecule falls above that of the unbranched. From Table 3 to Table 6, for backbone trifunctional-branched

macromolecules, we learn that for oblate branching, the b/ν values do not always exceed those of their unbranched counterparts. We also find that, for the prolate backbone trifunctional-branched Macromolecule 12, the b/ν fall below that of its unbranched counterpart.

We can deepen our understanding of the quantity b/ν by considering the shish-kebab, for which analytical expressions for b and ν are well-known. Using Table 14 from [9], we look at how b/ν changes with N , the number of beads on a shish-kebab. We substitute the equations for b and ν from Table 14 from [9], to get:

$$\frac{b}{\nu} = \frac{N(N^2 - 1)}{120} \quad (69)$$

from which we learn that for the rigid dumbbell, $b/\nu = 1/20$, and for large N ,

$b/\nu \cong N^3/120$ (see Figure 2). Similarly, for planar star-branched macromolecules, with singly-beaded branches, whose branching is oblate:

$$\frac{b}{\nu} = \frac{N}{20}; 3 \leq N \leq 6 \quad (70)$$

$$\frac{b}{\nu} = \frac{N}{80 \sin^2 \frac{\pi}{N}}; N \geq 7 \quad (71)$$

Figure 2 compares Eqs. (70) and (71) with Eq. (69), from which we learn that Cole-Cole plots for star-branched macromolecules will lie inside those of their unbranched counterparts.

Figure 3 compares prolate and oblate branched macromolecules with their common unbranched counterpart. The prolate Cole-Cole plot falls below its 5-bead unbranched counterpart, the oblate falls above.

a. COMPLEX MODULUS VERSUS VISCOSITY

Rewriting Eqs. (32) and (24) in terms of complex modulus:

$$\Gamma'' \equiv \frac{G''}{nkT} \equiv \frac{\omega \eta'}{nkT} = \frac{a\nu}{2} \lambda \omega \left\{ 1 + \frac{2b}{a\nu} \left(\frac{1}{1 + (\lambda \omega)^2} \right) \right\} \quad (72)$$

$$\Gamma' \equiv \frac{G'}{nkT} \equiv \frac{\omega \eta''}{nkT} = \frac{a\nu}{2} \lambda \omega \left\{ \frac{2b}{a\nu} \frac{\lambda \omega}{1 + (\lambda \omega)^2} \right\} \quad (73)$$

We next derive the Cole-Cole parametric relations. Solving Eq.(73):

$$\lambda \omega = \sqrt{\frac{\Gamma'}{b} \left(1 - \frac{\Gamma'}{b} \right)^{-1}} \quad (74)$$

Substituting this into Eq. (72):

$$\Gamma'' = \sqrt{\left(\frac{a\nu}{2} \right)^2 \left(\frac{1}{b - \Gamma'} + b \right)} \Gamma' - \Gamma'^2 \quad (75)$$

which is not circular, and which is subject to:

$$\left(\frac{av}{2}\right)^2 \left(\frac{1}{b-\Gamma'} + b\right) \geq \Gamma' \quad (76)$$

and Eqs. (26) through (29) become:

$$\Gamma''_0 \equiv \frac{\omega\eta_0}{nkT} \equiv \lim_{\lambda\omega \rightarrow 0} \Gamma'' = 0 \quad (77)$$

$$\Gamma'_0 \equiv \frac{\omega\eta''_0}{nkT} \equiv \lim_{\lambda\omega \rightarrow 0} \Gamma' = 0 \quad (78)$$

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

$$\Gamma''_\infty \equiv \frac{\omega\eta'_\infty}{nkT} \equiv \lim_{\lambda\omega \rightarrow \infty} \Gamma'' = \infty \quad (79)$$

$$\Gamma'_\infty \equiv \frac{\omega\eta''_\infty}{nkT} \equiv \lim_{\lambda\omega \rightarrow \infty} \Gamma' = \infty \quad (80)$$

Eq. (75) expands as:

$$\Gamma'' = \frac{1}{b} \left(\frac{av}{2} \sqrt{b} \sqrt{b^2+1} \right) \sqrt{\Gamma'} - \frac{\sqrt{b} \sqrt{b^2+1} \left[b^2 - \frac{1}{4} a^2 v^2 \right]}{avb^2(b^2+1)} \sqrt[3]{\Gamma'} + \dots \quad (81)$$

from which we learn that the modulus Cole-Cole plot departs will be convex, as it should be.

Using Eqs. (22) and (23) from [9], we can simplify Eq. (75) for oblate and prolate branched molecules. Eq. (75) for oblate branching becomes:

$$\Gamma'' = \sqrt{\left(\frac{9-6b+\sqrt{15b}}{6} \right)^2 \left(\frac{1}{b-\Gamma'} + b \right) \Gamma' - \Gamma'^2} \quad (82)$$

and prolate branching becomes:

$$\Gamma'' = \sqrt{\left(\frac{9-6b-\sqrt{15b}}{6} \right)^2 \left(\frac{1}{b-\Gamma'} + b \right) \Gamma' - \Gamma'^2} \quad (83)$$

which *Figure 4* and *Figure 6* illustrate respectively (as do *Figure 5* and *Figure 7*).

V. RESULTS

In the five subsections to follow, we shall explore the roles played by the five most important aspects of architecture for backbone branched macromolecules. To construct the figures for these five subsections, we draw upon Table 4 through Table 6, Table IV of [8], along with Table V of [9] for the unbranched macromolecules, namely, shish-kebabs. In this way, we shall explore our main results: Eq. (62) for complex viscosity Cole-Cole plots, versus Eqs. (82) and (83) for complex modulus Cole-Cole plots.

a. UNBRANCHED

Figure 8 illustrates how the number of beads on the backbone, N , reshapes the viscosity Cole-Cole plots for shish-kebabs (from Eq. (62) with Table V of [9]). We see that the circle radii increase with N . For all of the molecular architecture investigations in the four subsections to follow, we use the 5-bead backbone (**black** circle on *Figure 8*) to which branching is added. *Figure 9* illustrates how the number of beads on the

backbone, N , does not reshape the modulus Cole-Cole plots for shish-kebabs (from Eq. (83) with Table V of [9]).

b. NUMBER OF BRANCHES

Figure 10 illustrates the effect of number of branches on the viscosity Cole-Cole plots (from Eq. (62) with Table V of [8]). We see that the circle radii increase with the number of branches. *Figure 11* illustrates how the number of branches on the backbone reshapes the modulus Cole-Cole plots (from Eqs. (82) and (83) with Table IV of [8]). From *Figure 11* we learn that branching amplifies the modulus Cole-Cole plot. However, it does not do so monotonically. The trifunctional oblate branching curve falls above the quadrafunctional.

c. BRANCH LENGTH

Figure 12 illustrates the effect of branches length on the viscosity Cole-Cole plots (from Eq. (62) with Table 4). We see that the circle radii increase with branch length. *Figure 13* illustrates how the branch length on the backbone reshapes the modulus Cole-Cole plots (from Eq. (82) with Table 4). From *Figure 13* we learn that for oblate branching, branch length attenuates the modulus Cole-Cole plot.

d. BRANCH POSITION

Figure 14 illustrates the effect of branch position on the viscosity Cole-Cole plots (from Eq. (62) with Table 5). We see that the circle radii decrease as the branch position diverges from the center of the 5-bead backbone. *Figure 15* illustrates how the branch lopsidedness reshapes the modulus Cole-Cole plots (from Eq. (82) with Table 5). Specifically, lopsidedness amplifies the modulus Cole-Cole plots.

e. BRANCH DISTRIBUTION

Figure 16 illustrates the effect of branch distribution on the viscosity Cole-Cole plots (from Eq. (62) with Table 6). We see that the circle radii decrease as the branches distribute away from the 5-bead backbone center. *Figure 17* illustrates how the branch distribution along the backbone reshapes the modulus Cole-Cole plots (from Eq. (82) with Table 6). Specifically, distributing the branches away from the 5-bead backbone center amplifies the modulus Cole-Cole plots.

VI. WORKED EXAMPLE POLYPROPYLENE

a. COMPLEX VISCOSITY

The real and imaginary parts of the complex viscosity measurements from [17] for the unbranched (uPP), short-chain branched (D1), and long-chain branched (D3) polypropylene samples were fit to Eq. (62) to determine b/ν and $nkT\lambda_0$, illustrated in *Figure 18*. The fitted value of b/ν for the unbranched material is:

$$\frac{b}{\nu} \cong 700.0 \quad (84)$$

Since the uPP is unbranched, we can insert Eq. (84) into Eq. (69) to get:

$$N \cong 43.80 \quad (85)$$

Since N is discrete:

$$N \cong 44 \quad (86)$$

so that, from Eq. (69), we get:

$$\frac{b}{v} \cong 709.5 \quad (87)$$

and then, refitting Eq. (87), get:

$$nkT\lambda_0 = 2.400 \text{ Pa} \cdot \text{s} \quad (88)$$

Figure 19 illustrates this refitting and shows that our main result, arrived at from the general bead-rod theory for a monodisperse suspension, can still explain the behavior of disperse systems, even quantitatively.

b. COMPLEX MODULUS

For unbranched polypropylene, even though the viscosity Cole-Cole plots (middle curve, Figure 18) can be explained by the shish-kebab, the corresponding modulus plots cannot, illustrated in Figure 20 or, on log-log scales, in Figure 21. Fitting Eq. (83) to the observations for the unbranched material in Figure 20 yields $b \cong 100.0$ which differs markedly with the value for all shish-kebabs, $b = 3/5$.

We think the dispersity of our unbranched polypropylene may explain this (see Fig. 3. of [2]). Rewriting Eqs. (32) and (24) for a dispersed system of S species (see Problem 14C.2 of [15]; see also §26. of [18]):

$$\frac{\eta'}{nkT\lambda_0} = \frac{G''}{\omega nkT\lambda_0} = 6 \sum_{i=1}^S a_i \left\{ 1 + \left[\frac{2b}{av} \right]_i \left(\frac{1}{1 + (\lambda_i \omega)^2} \right) \right\} \quad (89)$$

$$\frac{\eta''}{nkT\lambda_0} = \frac{G'}{\omega nkT\lambda_0} = 6 \sum_{i=1}^S a_i \left[\frac{2b}{av} \right]_i \left(\frac{\lambda_i \omega}{1 + (\lambda_i \omega)^2} \right) \quad (90)$$

so that η'' and η' are parametric in ω , and thus, η'' is no longer explicit in η' .

Similarly, G' and G'' are also parametric in ω , and thus, G' is no longer explicit in G'' . In this context, the Spriggs relations (see §3.1.2 of [19]) may be used to reduce the number of constants from infinity to three. We leave this evaluation of mixtures of macromolecules for another day.

VII. CONCLUSION

Using general bead-rod theory, we have explained how oblate branching raises the viscosity Cole-Cole plot (Figure 8). However, to then use viscosity Cole-Cole plots to quantify branching content, one must control the branch functionality (Figure 10), length (Figure 12), position (Figure 14), and distribution along the backbone (Figure 16).

Using general bead-rod theory, we have also explained how oblate branching amplifies the modulus Cole-Cole plot (Figure 9). However, to then use modulus Cole-Cole plots to quantify branching content, one must control the branch functionality (Figure 11), length (Figure 13), position (Figure 15), and distribution along the backbone (Figure 17).

Comparing Subsection VI.b. with VI.a. of our worked example, at least for polypropylene melts, we learn that our monodisperse analysis of complex viscosity Cole-Cole plots [Eq. (62)] appears to be much more useful (even for dispersity) than our monodisperse analysis of complex modulus [Eq. (83)]. Arriving a suitable data, from the literature for our worked example was not easy because Cole-Cole plots are normally

published without their nonparametric counterparts, η' and η'' *versus* angular frequency, ω . Going forward, we would advise against this.

We focused on the Cole-Cole plots for the complex viscosity, but in small-amplitude oscillatory shear flow, polymeric liquids also respond with normal stress differences [Eqs. (18) and (19)]. It would be interesting to explore the effect of branching on the Cole-Cole plots constructed from the real and (minus) imaginary parts of the oscillating components of the first and second normal stress coefficients (Eqs. (22) through (24) of [20]). We leave this exploration for another day.

VIII. DATA AVAILABILITY

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

IX. 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. (8)]	M/t	ζ
Cartesian coordinates with respect to the center of mass	L	$\hat{\delta}_1, \hat{\delta}_2, \hat{\delta}_3$
Complex viscosity	M/Lt	η^*
Complex viscosity magnitude	M/Lt	$ \eta^* $
Displacement of viscosity Cole-Cole curve	L	x_c
Elastic modulus	M/L	G'
Element for Kronecker delta, [Eq. (1)]	t^{-1}	$\delta(s)$
Energy values in molecular-scale systems	ML^2/t^2	kT
First normal stress coefficient, small amplitude oscillatory shear response, displacement term [Eqs. (18) and (19)]	M/L	Ψ_1^d, Ψ_2^d
First/ second normal stress coefficient, in-phase with shear rate, for small amplitude oscillatory shear response	M/L	Ψ_1', Ψ_2'
First/ second normal stress coefficient, out-of-phase with shear rate, for small amplitude oscillatory shear response	M/L	Ψ_1'', Ψ_2''
First/second normal stress coefficient	M/L	Ψ_1^*, Ψ_2^*
Loss modulus	M/L	G''
Mass of each bead	M	m_i
<i>Minus</i> imaginary part of non-linear complex viscosity	M/Lt	η''
Molecular weight, number-average	M / mole	$\bar{M}_n$
Molecular weight, weight-average	M / mole	$\bar{M}_w$

Moments of inertia, (Eqs. (91) through (92) of [8])	ML^2	I_1, I_2, I_3
Normal stress differences [Eqs. (17) through (19)]	M/Lt^2	$\tau_{21}, \tau_{11}, \tau_{22},$ τ_{33}
Number of dumbbells per unit volume	$1/L^3$	n
Polymer contribution to the stress tensor	M/Lt^2	τ_p
Radius of viscosity Cole-Cole curve	L	R
Rate of deformation tensor	t^{-1}	$\dot{\gamma}(t)$
Rate-of-strain tensor	t^{-1}	$\dot{\gamma}$
Real part of non-linear complex viscosity	M/Lt	η'
Relaxation time of rigid dumbbell, [Eq. (9)]	t	λ_0
Relaxation time of solution, Eq. (7)	t	λ
Shear rate	t^{-1}	$\dot{\gamma}(t)$
Shear rate amplitude	t^{-1}	$\dot{\gamma}^0$
Shear rate at specific time t' , [Eq. (12)]	t^{-1}	$\dot{\gamma}(t')$
Shear relaxation function, [Eq. (1)]	M/Lt^2	$G(s)$
Solvent viscosity	M/Lt	η_s
Specific time, [Eq. (12)]	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	Range
Bead volume fraction [Eq. (10)]	φ	≥ 0
Coefficient in [Eq. (3)]	a	≥ 0
Coefficient in [Eq. (4)]	b	≥ 0
Coefficient in [Eq. (5)]	v	≥ 0
Deborah number, oscillatory shear	$De \equiv \lambda\omega$	≥ 0
Elastic modulus	Γ'	≥ 0
Imaginary part of the complex viscosity, [Eq. (44)]	H''	≥ 0
Loss modulus	Γ''	≥ 0
Real part of the complex viscosity, [Eq. (44)]	H'	≥ 0
Total number of beads	N	≥ 0
Weissenberg number	$Wi \equiv \lambda\dot{\gamma}^0$	≥ 0

Table 3: Effect of the number of branches (prolate branching).

	Macromolecule	$\frac{I_1}{mL^2}, \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{b}{\nu}$	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
1		10	0	$\frac{4}{3}$	$\frac{3}{5}$	$\frac{3}{5}$	1	$\frac{3}{2}$	20
12		$\frac{23}{2}$	3	$\frac{2123}{690}$	$\frac{867}{2645}$	$\frac{12}{23}$	$\frac{289}{460}$	$\frac{867}{2645}$	$\frac{26}{23}$

Table 4: Effect of branch length (oblate branching).

	Macromolecule	$\frac{I_1}{mL^2} \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{b}{\nu}$	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
2		$\frac{185}{2}$	165	$\frac{10427}{222}$	$\frac{2523}{6845}$	$\frac{12}{185}$	$\frac{841}{148}$	$\frac{2523}{10427}$	185
4		$\frac{293}{2}$	273	$\frac{637163}{8790}$	$\frac{192027}{429245}$	$\frac{12}{293}$	$\frac{18754637}{1716980}$	$\frac{576081}{1380866}$	293
5		220	420	$\frac{3530}{33}$	$\frac{60}{121}$	$\frac{3}{110}$	$\frac{200}{11}$	$\frac{120}{353}$	440

Table 5: Effect of branch position (oblate branching).

	Macromolecule	$\frac{I_1}{mL^2} \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{b}{\nu}$	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
2		$\frac{185}{2}$	165	$\frac{10427}{222}$	$\frac{2523}{6845}$	$\frac{12}{185}$	$\frac{841}{148}$	$\frac{2523}{10427}$	185
6		$\frac{215}{2}$	165	$\frac{14753}{258}$	$\frac{1587}{9245}$	$\frac{12}{215}$	$\frac{529}{172}$	$\frac{1587}{14753}$	215
7		$\frac{297}{2}$	165	$\frac{2299}{30}$	$\frac{1}{135}$	$\frac{4}{99}$	$\frac{11}{60}$	$\frac{1}{209}$	297

Table 6: Effect of branch distribution (oblate branching).

	Macromolecule	$\frac{I_1}{mL^2} \frac{I_2}{mL^2}$	$\frac{I_3}{mL^2}$	a	b	ν	$\frac{b}{\nu}$	$\frac{2b}{a\nu}$	$\frac{\lambda}{\lambda_0}$
2		$\frac{185}{2}$	165	$\frac{10427}{222}$	$\frac{2523}{6845}$	$\frac{12}{185}$	$\frac{841}{148}$	$\frac{2523}{10427}$	185
8		$\frac{205}{2}$	165	$\frac{13295}{249}$	$\frac{375}{1681}$	$\frac{12}{205}$	$\frac{625}{164}$	$\frac{375}{2659}$	205
9		$\frac{235}{2}$	165	$\frac{17717}{282}$	$\frac{1083}{11045}$	$\frac{12}{235}$	$\frac{361}{188}$	$\frac{1083}{17717}$	235
10		$\frac{265}{2}$	165	$\frac{22283}{318}$	$\frac{507}{14045}$	$\frac{12}{265}$	$\frac{169}{212}$	$\frac{507}{22283}$	265

Figure 1: Dimensionless Cole-Cole plot of Eq. (62) over the b/v range of Eq. (63) where $b/v = 1$ (red), $b/v = 10$ (green), and $b/v = 20$ (blue).

Figure 2: Dimensionless plot to determine how b/v is effected by the number of beads, N , for a shish-kebab from Eq. (69) (blue), star-branched when $3 \leq N \leq 6$ from Eq. (70) (red) and star-branched when $N \geq 7$ from Eq. (71) (green).

Figure 3: Dimensionless Cole-Cole plot of Eq. (62) comparing short-chain branched Macromolecule 12 (blue) with long-chain branched Macromolecule 2 (red) versus unbranched Macromolecule 1 (black) from Table 3 and Table 4. All macromolecules have the same backbone length (5 beads).

Figure 4: Dimensionless modulus linear Cole-Cole plot (also known as the Han plot ([17], [21], [22]) for oblate branching of Eq. (82) over the b range of Eq. (6) where $b = 1/10$ (black), $b = 1/5$ (red), $b = 3/10$ (green), $b = 2/5$ (blue), $b = 1/2$ (cyan) and $b = 3/5$ (magenta).

Figure 5: Dimensionless modulus log-log Cole-Cole plot (also known as the Han plot ([17], [21], [22]) oblate branching of Eq. (82) over the b range of Eq. (6) where $b = 1/10$ (black), $b = 1/5$ (red), $b = 3/10$ (green), $b = 2/5$ (blue), $b = 1/2$ (cyan) and $b = 3/5$ (magenta).

Figure 6: Dimensionless modulus linear Cole-Cole plot (also known as the Han plot ([17], [21], [22]) for prolate branching of Eq. (83) over the b range of Eq. (6) where $b = 1/10$ (black), $b = 1/5$ (red), $b = 3/10$ (green), $b = 2/5$ (blue), $b = 1/2$ (cyan) and $b = 3/5$ (magenta).

Figure 7: Dimensionless modulus log-log Cole-Cole plot (also known as the Han plot ([17], [21], [22]) prolate branching of Eq. (83) over the b range of Eq. (6) where $b = 1/10$ (black), $b = 1/5$ (red), $b = 3/10$ (green), $b = 2/5$ (blue), $b = 1/2$ (cyan) and $b = 3/5$ (magenta).

Figure 8: Effect of chain length on complex viscosity Cole-Cole plots for unbranched macromolecules, namely shish-kebabs, from Eq. (62) with Table V of [9].

Figure 9: Effect of chain length on complex modulus Cole-Cole plots for unbranched macromolecules, namely shish-kebabs, from Eq. (83) with Table V of [9].

Figure 10: Effect of the number of branches on complex viscosity Cole-Cole plots for oblate branched macromolecules from Eq. (62) with Table IV of [8].

Figure 11: Effect of the number of branches on complex modulus Cole-Cole plots for oblate branched macromolecules from Eqs. (82) and (83) with Table IV of [8].

Figure 12: Effect of branch length on complex viscosity Cole-Cole plots for oblate branched macromolecules from Eq. (62) with Table 4.

Figure 13: Effect of branch length on complex modulus Cole-Cole plots for oblate branched macromolecules from Eq. (82) with Table 4.

Figure 14: Effect of branch position on complex viscosity Cole-Cole plots for oblate branched macromolecules from Eq. (62) with Table 5.

Figure 15: Effect of branch position on complex modulus Cole-Cole plots for oblate branched macromolecules from Eq. (82) with Table 5.

Figure 16: Effect of branch distribution on complex viscosity Cole-Cole plots for oblate branched macromolecules from Eq. (62) with Table 6.

Figure 17: Effect of branch distribution on complex modulus Cole-Cole plots for oblate branched macromolecules from Eq. (82) with Table 6.

Figure 18: Dimensionless Cole-Cole plot of formulations D1 (red), uPP (green) and D3 (blue) from [17] being fit to Eq. (62) over the b/ν range of Eq. (63) resulting in estimates of $b/\nu = 545.0$, $nkT\lambda_0 = 2.500 \text{ Pa} \cdot \text{s}$ for D1, $b/\nu = 700.0$, $nkT\lambda_0 = 2.500 \text{ Pa} \cdot \text{s}$ for uPP and $b/\nu = 830.0$, $nkT\lambda_0 = 3.000 \text{ Pa} \cdot \text{s}$ for D3.

Figure 19: Refitting of the dimensionless Cole-Cole plot to Eq. (87) for unbranched polypropylene (uPP) for $N \cong 44$, $b/\nu = 709.5$, and $nkT\lambda_0 = 2.400 \text{ Pa} \cdot \text{s}$.

Figure 20: Dimensionless complex modulus Cole-Cole plot of formulations uPP (blue), D1 (red), and D3 (green) from [17] being fit to Eq. (82) and (83), resulting in estimates of $b = 30.00$, $nkT = 10.00\text{Pa}$ for uPP, $b = 27.00$, $nkT = 15.00\text{Pa}$ for D1, and $b = 30.00$, $nkT = 14.50\text{Pa}$ for D3.

Figure 21: Dimensionless complex modulus Cole-Cole log-log plot of formulations uPP (blue), D1 (red), and D3 (green) from [17] being fit to Eq. (82) and (83), resulting in estimates of $b = 30.00$, $nkT = 10.00\text{Pa}$ for uPP, $b = 27.00$, $nkT = 15.00\text{Pa}$ for D1, and $b = 30.00$, $nkT = 14.50\text{Pa}$ for D3.

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