Rheo-Optical Evidence of CCR in an Entangled Four-Arm Star

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ABSTRACT: We present a model to describe the response of entangled star polymers to steady shear flow. The central ingredient of this model is the inclusion, in a simplified way, of convective constraint release once the shear rate reaches the inverse of the longest relaxation time. Rheo-optical measurements for a solution of four-arm polybutadiene stars demonstrate the efficacy of this model in capturing the salient features of the stars' response as measured by the shear stress and first normal stress difference. These results demonstrate the necessity of including convective constraint release in any model used to describe the nonlinear behavior of stars. Models and experimental results for flows of stars other than steady shear are the subject of ongoing work.

1. Introduction

In recent years, there has been considerable progress in developing molecular models for describing the behavior of entangled polymers systems.[1−4] In the linear viscoelastic regime, the storage and loss moduli can be accurately predicted for a wide range of architectures knowing only the degree of entanglement, the plateau modulus, G_N^0, and the relaxation time of an entanglement segment, τ_e. The degree of entanglement can be found knowing the polymer molecular weight measured using size exclusion chromatography and the molecular weight of an entanglement found in the literature. For a melt, the two material parameters are readily found in the literature, however for a solution the best results come from measuring these two parameters directly.[5]

In the nonlinear regime the same degree of success has not quite been reached. However, several recent models have been able to capture qualitatively and sometimes quantitatively the response of different linear and branched polymer systems to flow.[2,3,6,7] Many of the proposed constitutive relations used to describe linear polymers have incorporated the relaxation mechanism known as convective constraint release (CCR), where entanglements with neighboring chains are thought to be released via the relative motion produced by continual retraction from the stretched configuration that would be produced by affine deformation with the flow. The inclusion of this mechanism eliminates the unrealistic maximum of shear stress vs shear rate that is predicted by the original Doi−Edwards model.[8]

More recently, attention has turned to branched polymers, as they represent a further degree of complexity, and a step toward the polymers that are commonly found in industrial use. Star polymers, the simplest of the branched polymers, have been thoroughly explored in the linear viscoelastic regime, but relatively few in depth studies of their response to flow have yet been carried out. Stars provide an ideal framework for unequivocally demonstrating the existence of convective constraint release. This is because the available relaxation mechanisms produce such a broad spectrum of relaxation times that the onset of CCR is expected to be the first significant departure from the linear viscoelastic relaxation processes, and then to be completely dominant up to shear rates of O (τ_R^{-1}).

Because the star has a single branch point at its center, reptation is suppressed and the arm must relax by repeated explorations of the free end within the tube. The result is that the longest linear relaxation time for the star is *exponentially* dependent on the arm molecular weight, rather than the power law relation found for linear polymers. There is a large experimental window where the shear rate is between the inverse of the longest relaxation time, where flow is expected to play an increasing role, and the inverse of the Rouse time, where the onset of chain stretching is found. If convective constraint release can be used in the model for stars as it has previously been for linear polymers, it should clearly manifest itself in this range of shear rates as the dominant relaxation mechanism.

One other point of interest is the question of whether the process of convective constraint release is sensitive to the polymer architecture. One presumes, on the basis of current ideas, that it should occur in essentially the same way for the arms of a star and for a linear chain. This is because the release of constraints from neighboring chains generates Rouse-type dynamics of the tube containing unrelaxed chain. Rouse dynamics are only weakly dependent on architecture globally, and locally independent. If this is the case, we should expect the model for linear chains to work well for stars without change of the numerical prefactors, but modified in a way that reflects the great range of linear relaxation time scales along the star arm. In one aspect this feature actually simplifies the modeling: the exponentially extended relaxation times of entangled stars make it much easier to separate the orientation and stretch regimes of flow as a function of deformation rate. So models of CCR without stretch will be adequate for our treatment

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2. Experiments

2.1. Materials. A 1,4-polybutadiene four-arm star was prepared using anionic techniques with a chlorosilane linking agent. The product was purified by fractional precipitation until unreacted linear arms were removed. The linear precursor arms and final star melt were characterized using SEC-GPC. The GPC measurement was made using polystyrene standards and corrected using the measured intrinsic viscosity of the polybutadiene samples along with the Mark−Houwink expression.[9,10] The correction factor (M_{PS}/M_{PB}) was different for the linear (1.6) and star architectures (1.25). The molecular weight of the purified star was 240 000 and the PDI was 1.08. Special care was taken to ensure optical clarity of the final product. Using NMR the synthesized polybutadiene was found to be 9% 1,2 addition and 91% 1,4 addition, with half of that being of the cis conformation and the other half being of the trans conformation. Then 0.1 wt % of antioxidant (2,6-di-*tert*-butyl-*p*-cresol) was added to minimize sample degradation. The star was put into solution in tetradecane at 20 wt %.

2.2. Methods. The star melt and solution were characterized using a Rheometric Scientific strain controlled ARES rheometer with a temperature controlled convection oven. Strain sweeps were conducted to find the range of stable conditions for a range of frequencies. Frequency sweeps were then carried out over a range of temperatures and then using time−temperature superposition shifted to 22 °C with frequencies ranging from 0.01 to 100 rad/s to obtain the linear viscoelastic response (G', G'').

Rheo-optical experiments were carried out using a two-color flow birefringence apparatus at room temperature as originally described by Chow and Fuller.[11] The sample was loaded into a small shear cell for study. An argon laser was used to output blue and green beams that were polarized at a relative angle of 45°. The beams were simultaneously passed through the same point in the sample and then through an analyzer oriented at 90° from the initial polarization of each color. This experimental setup allows the direct measurement of the degree of optical anisotropy, or the birefringence, Δn, and the orientation angle, χ, of the polymer solution as it is sheared at various rates.[12,13]

3. Results and Discussion

Current models are thoroughly capable of describing the behavior of entangled stars in the linear viscoelastic regime.[14,15] Stars can be modeled similarly to linear polymers using the "tube" model originally developed by Doi and Edwards. However, because of their branch point, reptation is strongly inhibited. In the linear viscoelastic regime, arms relax independently and primarily by contour length fluctuations (CLF), as the free end of each arm fluctuates down its tube and then is free to extend out in a new direction. As segments relax and are no longer able to hold entanglements they begin to behave as solvent, diluting the remaining entanglements in a process called dynamic dilution. A normalized curvilinear coordinate, s, can be defined along the length of the star arm with $s = 0$ at the free end and $s = 1$ at the branch point. Using CLF and dynamic dilution, the relaxation time for the linear viscoelastic regime at each point, s, along the star arm can be defined using the following theoretical description.[15] (Here we use the definition-set of entanglement spacing and moduli that include the prefactor of $^4/_5$ in the plateau modulus.)[16]

First the rapid relaxation of the arm ends by Rouse like motion can be characterized by a characteristic time scale:

$$\tau_{early} = \frac{9}{16}\pi^3 Z^4 s^4 \tau_e \qquad (1)$$

Here Z is the number of entanglements per arm and τ_e is the intrinsic relaxation time of an entanglement segment. On the other hand deep retractions of the arms are characterized by the relaxation time:

$$\tau_{arm} = \sqrt{\frac{\pi^5}{6}}\tau_e Z^{3/2}\frac{e^{U_{eff}(s)}}{\left(s^2(1-s^2)+\frac{2}{3\pi Z}\right)^{1/2}} \qquad (2)$$

$U_{eff}(s)$ is an effective potential that includes the effects of both CLF and dynamic dilution

$$U_{eff}(s) = \frac{15}{4}Z\left(\frac{s^2}{2}-\frac{s^3}{3}\right) \qquad (3)$$

An expression that can be used to describe a smooth transition from one time scale to the other is then used to describe the relaxation time at each point along the star arm:

$$\tau(s) = \frac{\tau_{early}}{e^{-U_{eff}(s)}+\frac{\tau_{early}}{\tau_{arm}}} \qquad (4)$$

Using this relation for the relaxation of the arms, the plateau modulus of the polymer (G_N^0), and a dilution exponent, α, of 1 the modulus can be calculated as

$$G(t) = G_N^0(1+\alpha)\int_0^1 ds\,(1-s)^\alpha \exp[-t/\tau(s)] \qquad (5)$$

For melts of stars, this series of equations has been demonstrated to accurately describe the linear viscoelastic spectra of the storage and loss moduli, G' and G'', which can be calculated by taking the Fourier transform of $G(t)$ with only the two material parameters: G_N^0 and τ_e.[17]

In the nonlinear regime the relative motions of polymer chains must be considered. The concept of a convective constraint release relaxation mechanism was originally proposed by Marrucci as a way to account for the orientational relaxation of a test chain as the flow-induced motion of neighboring chains along with chain retraction brought about the removal of entanglements.[8,18] In later studies, a microscopic theory of CCR was proposed to describe the effects of CCR on tube conformation in terms of an effective Rouse motion of the tube.[19] In this paper we propose a simple model to describe the behavior of entangled stars under steady shear. This model includes CCR in an asymptotic limit, exploiting the strong separation of time scales along the star arm. This approach is meant to test the hypothesis that the effects of CCR will be dominant and apparent in both the shear stress and first normal stress difference of the entangled stars at sufficient shear rates. The model is limited to shear rates less than the inverse of the Rouse time because it does not include any effects from chain stretching. Furthermore, it is also applicable only to steady-state response: a full theory of CCR adapted for star architectures will be required to handle transient response.

Consider a point on the star arm, s^*, defined such that the shear rate multiplied by the relaxation time at that point is unity ($\dot\gamma\tau(s^*) = 1$). Then the star is divided into two parts: the end segments ($0 \le s < s^*$) that possess relaxation rates much faster (typically exponentially) than the flow and the interior segments ($s^* \le s \le 1$)

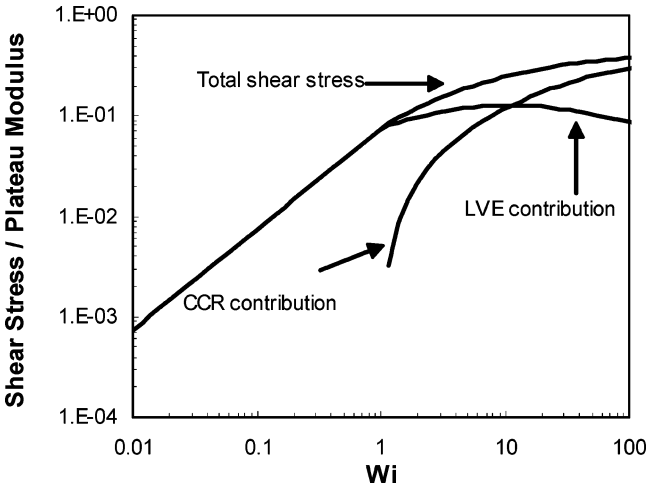

Figure 1. Plot of shear stress normalized by plateau modulus vs Weissenberg number (shear rate times the longest relaxation time) divided into two separate components. The addition of convective constraint release (the second term on the right-hand side of eq 6b) eliminates the shear stress maximum of the linear viscoelastic contribution from Doi−Edwards theory (eq 6a).

whose relaxation rates are much slower. The end part is relaxed essentially before it feels the flow and thus can be described by the model that has been developed for the linear regime (it is in local linear response). The interior regions are not yet relaxed by contour length fluctuations when they are influenced by the flow and so, in the absence of CCR (or, in principle, other relaxation mechanisms), they would be fully aligned in the flow direction. This produces a contribution to the first normal stress difference, but no contribution to the shear stress. Thus, without CCR, the shear stress is simply standard linear response transformed to steady shear flow.

$$\sigma_{12} = \dot{\gamma} G_N^0 \int_0^{s^*(\dot{\gamma})} \tau(s)(1 - s)\, ds \tag{6a}$$

However here, the integral, instead of going from zero to one, goes only from zero to s^* because this relation is only relevant to the portion of the star that remains in the linear regime. For stars, the dominant relaxation mechanism is CCR. This acts uniformly over the interior portions of the chain to reduce the degree of alignment. We know that, in the absence of chain stretch, CCR produces a plateau in the shear stress at approximately 0.6 of the relevant plateau modulus.[19] By assuming that the relaxation processes for the two parts of the star arm act independently, an equation for the shear stress as a function of shear rate can be written as the sum of the two separate contributions:

$$\sigma_{12} = \dot{\gamma} G_N^0 \int_0^{s^*(\dot{\gamma})} \tau(s)(1 - s)\, ds + 0.6 G_N^0 (1 - s^*(\dot{\gamma}))^2 \tag{6b}$$

The second part of the equation is the contribution from CCR. For *linear* polymers the steady state shear stress was found to be approximately equal to 0.6 times the plateau modulus. Since the Rouse-like relaxation controlling the CCR-dominated plateau is dominated by local processes, this will also be true for the star arms. However, for stars there is the additional factor $(1 - s^*(\dot{\gamma}))^2$. The first of these terms accounts for dynamic dilution, and the second term occurs because only the interior part of the star is affected by the flow, and acts as a flow-rate dependent renormalization of the effective plateau modulus.

A corresponding equation for the first normal stress difference, N_1, can be written. Here there is no linear viscoelastic contribution from the outer part of the arms. In the absence of CCR, the interior regions of the arms are fully aligned in the flow direction, and this produces a first normal stress contribution, which after accounting for dynamic dilution and the relevant part of the chain, is

$$N_1 = 3.0 G_N^0 (1 - s^*(\dot{\gamma}))^2 \tag{7a}$$

The inclusion of CCR means that the interior portions of the arms are not completely aligned, and thus the magnitude of the normal stress contribution is reduced. Assuming again that the prefactor that was found to work best for linear polymers is still relevant for the star arms, the normal stress contribution is reduced by almost a factor of 2 to

$$N_1 = 1.55 G_N^0 (1 - s^*(\dot{\gamma}))^2 \tag{7b}$$

The factor of $(1 - s^*(\dot{\gamma}))^2$ is included for the same reasons outlined above.

For *linear* polymers, the inclusion of CCR resulted in the elimination of a shear stress maximum in the plot of shear stress vs steady shear rate or Weissenberg number. Since this shear stress maximum is not experimentally realizable, its elimination has been cited as one of the important successes of the CCR idea.[8] The same result is found in the case of stars. Figure 1 shows the two components of the shear stress. The first component comes from the fraction of the star described by the linear viscoelastic theory and shows a clear shear stress maximum. By adding in the contributing form of convective constraint release, this maximum is eliminated and the shear stress continues to increase monotonically with increasing shear rate.

The equations developed above are only relevant for steady shear. It is hypothesized that a similar adjustment of successful transient models for *linear* polymers may be useful in describing the transient behavior of stars, but that will be the subject of future work.

This model has been tested for a 20% solution of four-arm polybutadiene in tetradecane as described earlier. The resulting solution had 6.5 entanglements per arm based on the measured melt molecular weight (240 000), and the entanglement molecular weight for the solution, $M_e(\phi)$, which is calculated from the entanglement molecular weight of the melt M_{e0} (1850 g/mol),[20] and the weight fraction, ϕ, of the polymer (0.20) using a dilution exponent, α, of 1.

$$M_e(\phi) = \frac{M_{e0}}{\phi^{\alpha}} \tag{8}$$

The literature value for the plateau modulus was used (1.25 MPa),[20] and then τ_e was adjusted to find the best fit of the linear viscoelastic data for G'' with the theory presented previously. The resulting value for τ_e was $5 \times 10^{-7} s$. The focus on G'' to obtain τ_e is a consequence of the fact that the range of available frequencies are all quite low for this particular polymer solution and thus the linear viscoelastic data all falls below the crossing point for G' and G'', where G' values are small (~10 Pa) and in the range where the G' data are not

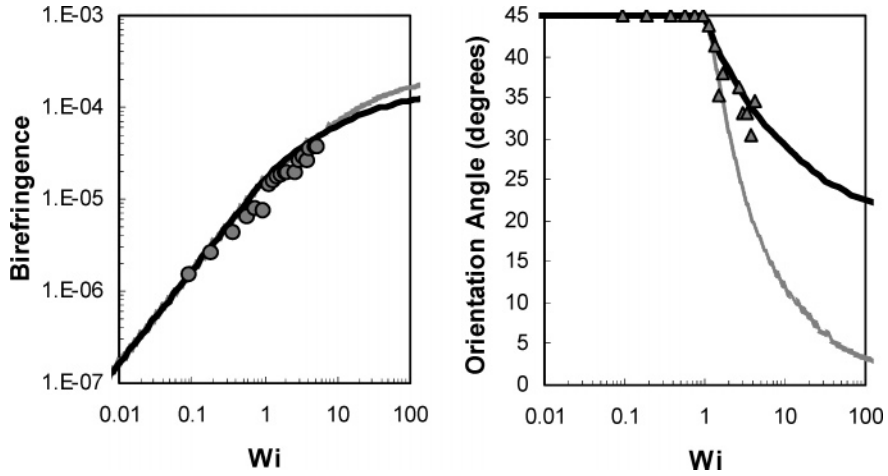

Figure 2. Comparison between model (dark line), the model without CCR (light line), and experiment (discrete points) for steady shear of a solution of entangled four arm polybutadiene stars. Plots show birefringence and orientation angle vs Weissenberg number (*Wi*), where the Weissenberg number is based on the longest relaxation time.

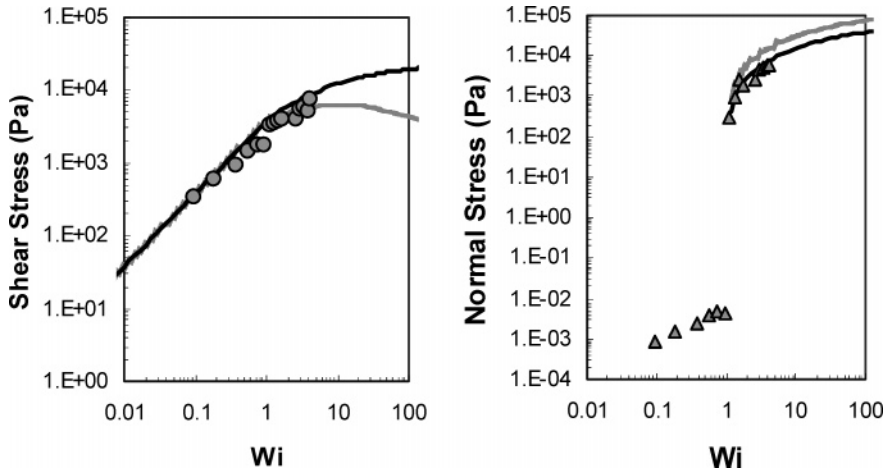

Figure 3. Comparisons between model (dark line), the model without CCR (light line) and experiment (discrete points) for the shear stress and first normal stress difference vs Weissenberg number for an entangled solution of four-arm polybutadiene stars.

very accurate. For other solutions with larger relaxation times (where accurate data is obtained for both G' and G'' both above and below the crossing point) this procedure of using the low-frequency data for G'' to estimate τ_e is found to produce excellent fits for both G' and G'' over the whole range of frequencies. From the best fit of the linear viscoelastic data, the longest relaxation time of the solution was found by setting $s = 1$ in the equation for $\tau(s)$ and the value was 0.019s. τ_R is found from $\tau_R = \tau_e Z^2$ and had a value of 2.1×10^{-5} s. Thus, this system belongs to the class in which orientation times and stretch times are well separated.

In the comparison between the experimental data for the steady shear experiments and model predictions there were no fitting parameters used. To calculate the birefringence and orientation angle predicted by the model, the stress optical rule was used. This rule is valid until changes occur in the polymer configuration which change the stress without producing a corresponding change in the birefringence, such as "nonlinear" chain stretching that is modified by finite extensibility. It is thus certainly valid for shear rates less than the inverse Rouse time, when chain stretching is thought to begin.[21] The literature value of the stress optical coefficient, C, was used, namely $C = 2.2 \times 10^{-9}$ m^2/N.[22] The birefringence and stress components are then related as

$$\sigma_{12} = \left(\frac{\Delta n}{2C}\right) \sin(2\chi) \tag{9}$$

$$N_1 = \sigma_{11} - \sigma_{22} = \left(\frac{\Delta n}{C}\right) \cos(2\chi) \tag{10}$$

Figure 2 shows measured values for the birefringence and orientation angle χ, compared with model predictions via eqs 6b, 7b, 9, and 10. Also shown in Figure 2 are the results predicted via the model equations, but without CCR (i.e., (6a), (7a), (9), and (10)). We can see that there is excellent agreement between the model incorporating CCR (i.e., eq 7b), and experiment for the range of Weissenberg numbers examined. Here the Weissenberg number is defined as the shear rate times the longest relaxation time. With CCR neglected, there is little change in the predicted birefringence, but the orientation angle increases at a significantly faster rate with increase of *Wi*, and agrees much less well with the experimental data than the model including CCR. Figure 3 shows the same data expressed in terms of σ_{12} and N_1 rather than birefringence and orientation angle. Again, we show model predictions both with and without CCR included. An expanded version of the plot of N_1 vs *Wi* is shown in Figure 4, to give a higher resolution of the comparison between the data and the model predictions. Again, it is evident that the inclusion of

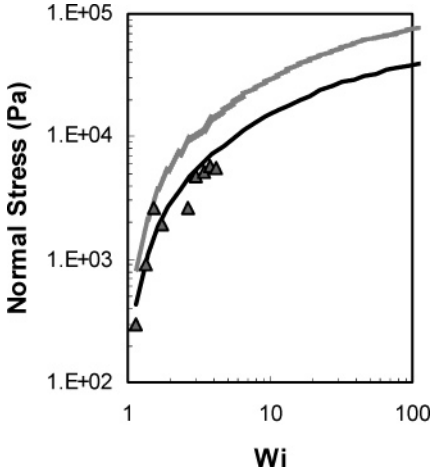

Figure 4. Expanded view of the comparison between experimental data and model predictions for normal stress. The solid line shows the model including CCR, with the prefactor of 1.55 (eq 7b) while the dashed line shows the comparable model without CCR and the resulting prefactor of 3 (eq 7a).

CCR yields predictions that are in excellent agreement with the data. Indeed, the comparisons in Figures 2−4 provide a strong case for the importance of CCR.

The model and experiment both show a fundamental change in behavior around a Weissenberg number of 1. It is here that the orientation angle first begins to deviate from 45°, which is the orientation of the principle strain rate axis. A decrease in the orientation angle indicates that the polymer is beginning to align toward the flow direction, at 0°. Without the inclusion of CCR, the linear contribution will always result in an orientation angle of 45°. Also, at a Weissenberg number of 1, there is a clear onset of a significant nonzero first normal stress difference as predicted by the model.

These results demonstrate that by merely including a simple form of convective constraint release, selected nonlinear phenomena can be qualitatively explained. It is significant that the prefactors for the terms representing the contribution of CCR were taken directly from the best fit of the model for *linear* polymers. The applicability of the same prefactors for stars may be interpreted as demonstrating the independence of CCR from chain architecture for entangled polymer systems, which in turn confirms its dominant role as a relaxation process local to a few entanglement strands.

4. Conclusions

Rheo-optical studies were conducted to investigate the response of a solution of entangled four-arm stars to steady shear. It was hypothesized that for Weissenberg numbers greater than 1, the flow induced relaxation mechanism of CCR would begin to dominate the stress response. To test this hypothesis, a simple model was created based upon the assumption of additive contributions to the stress from the outer portion of the arms which relax via the normal linear viscoelastic mechanism of arm retraction and expansion, and the inner portion of the arms where the relaxation process is dominated by CCR. In the absence of CCR, the inner parts of the arms would align in the flow direction, producing a contribution to N_1 but no contribution to the shear stress. The relaxation due to CCR competes against the tendency to align in the flow direction. This yields a contribution to the shear stress, and a reduction in the magnitude of N_1. Prefactors for the CCR contribution were taken directly from results of a molecular model for linear polymers. Good agreement between the experimental data and the model indicates that CCR is an essential ingredient in describing the response of entangled stars for $Wi > 1$. The success of CCR in describing these steady state experiments indicates that it must be included in any more complicated models if we hope to be able to accurately predict the transient and steady response of entangled stars to various flows.

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