Rheology of star-linear polymer blends: molecular tube models

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We apply the tube model to a specific problem in polymer melt dynamics — the rheology of star polymers as an additive to a monodisperse linear matrix. We find that the tube dilation picture of constraint release may be applied to the relaxation of the star fraction. There are four qualitatively different cases depending on the relative concentrations and relaxation times of the two fractions. Terminal relaxation times and relaxation spectra are calculated for each case. A comparison with experimental data is made in the case of dilute stars in a matrix of linear chains. This supports the theoretical prediction of a modified Rouse relaxation such that $G(t) \sim t^{-3/2}$.

(Keywords: rheology; melts; tube model; blends; topology)

INTRODUCTION

Some recent attention has been given to the question of star-branched polymers as rheological additives[1] to melts, particularly in the entangled regime. This is of interest in a number of processing procedures, for which branched polymers may act very efficiently as rheological modifiers. Another application arises in the case of a weakly crosslinked melt of linear polymers, in which very few molecules contain more than one branch point and nearly every crosslink forms the branch point of a star. Such a system is also of scientific interest because theoretical models applicable to the molecular dynamics of entangled branched polymers are now at hand[2–14]. The core idea in any entangled melt of concentrated solution is that the topological constraints on a molecule may be treated in an averaged way as a confining tube of radius a, centred on the molecule's contour[5]. The value of a is set by the plateau modulus of the melt. A molecule is free to move along the tube ('reptation') but is confined laterally.

The model is very successful in predicting the properties of monodisperse linear polymers. In some cases there is accurate quantitative agreement, such as the short-time non-linear response to a step-strain (the so-called 'damping function'). In the other cases the predictions of the basic model are more qualitative, such as the form of the time-dependent relaxation (near single exponential) and the molecular-weight dependence of the viscosity (theoretically M^3 and experimentally nearer $M^{3.4}$). Recent work on the contribution of the Rouse-like motion of the chain ends[15], ignored in the original treatment, indicates that this feature is likely to be the source of the latter discrepancies but understanding is still lacking in the case of only marginally entangled polymers.

The theory also needs extension whenever there are present chain segments whose configurational relaxations occur on different time-scales. The chief problem in understanding the rheology of these systems lies in the large 'constraint-release' mechanisms which affect both the linear and branched fractions. Now a segment of chain can relax either by motion along its own tube or by the relaxation of some of the topological constraints from neighbouring molecules. Constraint-release in blends of linear polymers is complex[6–10] and far from understood, but can sometimes be simplified in the case of branched polymers where 'tube dilation' is the dominant process[11–14]. The reason for the simplification is that the relaxation times of different parts of a star molecule are very well separated. We review the physical assumptions of this model next, then apply it to a model case of monodisperse star polymers in a monodisperse linear matrix, for which the simplifying features of the star melt will survive for regimes where the star fraction is important.

TUBE DILATION

This limiting case of constraint-release seeks a self-consistent calculation of tube dynamics by treating all polymer chain segments which relax on time-scales faster than a given time t as effective solvent fraction for any dynamics which occurs on the t time-scale[11–14]. It finds mathematical expression in some hierarchical equation which expresses the dynamics of slower processes in terms of faster ones, and involving a renormalized effective concentration. The method is thus ideally suited to the tube dynamics of branched polymers which exhibit a hierarchy of relaxation time-scales from the fast free ends of the chains to the slow segments near the branch points.

Stress relaxation proceeds via sequential arm retraction (*Figure 1*). This causes fluctuations in the entangled path length which are equivalent to the Brownian diffusion of a particle in a potential well whose minimum rests at the mean entangled path length. Thus the segments along a star arm of molecular weight M_a of contour co-ordinate

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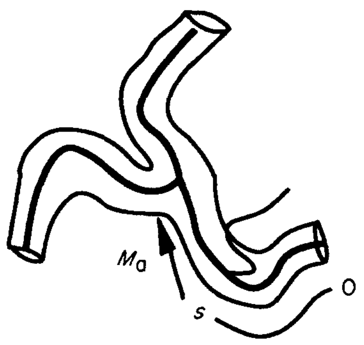

Figure 1 Contour co-ordinate s for an entangled star polymer in an effective tube. Disentanglement proceeds via rare retractions such as the one shown by the light line

s $(0<s<M_a)$ have relaxation times $\tau(s)$ given by:

$$\frac{d\tau(s)}{ds}=\tau(s)\alpha\left(\frac{s}{M_a}\right)C_{net}[\tau(s)] \qquad (1)$$

where $\alpha=15M_a/4M_e$ and M_e is the bare entanglement molecular weight of the polymer[11-14]. The equation describes thermally activated diffusion of the particle (representing the free end of the polymer) in the arc-length co-ordinate, s, along its tube. The effective potential $U(s)$ working against this diffusion is quadratic to a good approximation. The right-hand side of equation (1) is proportional to dU/ds, so is linear in s. The last term of equation (1), $C_{net}(\tau)$, is the effective concentration of unrelaxed segments, or the concentration of an effective network for the sequential relaxation. It describes the accelerating effect on the dynamics of slow segments due to their dilution by faster ones and acts on the effective potential $U(s)$ to make it dependent on the time-scale of the motion. The effective concentration appears to the first power as a consequence of either the ansatz that entanglements are two-body interactions of chains or of the experimental finding that the effective entanglement molecular weight varies as the inverse first power of concentration in concentrated polymer solutions. This is equivalent to a variation in tube diameter such that $a\sim C^{-1/2}$.

The concentration of unrelaxed segments proceeds stochastically as a function of time but must be consistent with the relaxation times calculated in equation (1). Taking an ensemble average over all fluctuating arms gives:

$$C_{net}(t)=\int_0^{M_a} e^{-t/\tau(s)}\,ds \qquad (2)$$

which completes the system of tube dilation equations for monodisperse branched polymers. As they stand they present a non-linear integral equation, so do not give any obvious advantage over other methods of treating constraint-release which consider the detail of the motion of the effective tube[6-10]. However, the expression for C_{net} may be further approximated using the fact that for $\alpha\gg 1$ (the interesting limit of well entangled arms) the integrand of equation (2), $e^{-t/\tau(s)}$, is very close to a step-function in s for any time t, so that $C_{net}(t)\approx[1-s(t)/M]$.

Equations (1) and (2) together constitute an approximation to the full diffusion equation for the free end valid in the limit of large α, and correctly captures the exponential dependence of relaxation times on arc co-ordinate. The longest relaxation time, for instance, $t(M_s)$ is $t_0\exp(\alpha/6)$ where t_0 is the relaxation time for length fluctuations and is of the order of the Rouse time for the free polymer.

The hierarchical dynamics are supplemented by an assumption for the calculation of the stress due to the dynamic network. This must be consistent with the scheme for the dynamics. The usual assumption due to Marrucci[6] is to take:

$$G(t)=G_0[C_{net}(t)]^{\gamma} \qquad (3)$$

where γ is an exponent describing the effect of dilution on the plateau modulus, G_0. The value of γ in good solvents is understood from scaling arguments to be 9/4, which is in good accord with experiments. In θ solvents and concentrated solutions the experimental value is also close to two, and Colby and Rubinstein[16] claim evidence in support of a scaling value of 7/3. In this work we leave open the exact choice of γ and express results in terms of the effective network.

The theoretical treatment described above accounts very successfully for the linear frequency-dependent rheology of monodisperse star polymers. Ball and McLeish using this procedure predicted $G(t)$ to within a factor of 2 over 10 decades in frequency for the polystyrenes of Pearson and Helfand such that $\alpha>20$, requiring only that the fundamental monomeric relaxation time be fitted from the data[11-14]. This was an important step for, although the previous theoretical treatments of star polymers in melts without constraint-release[6-10] successfully accounted for the exponential dependence of the viscosity and for the approximate form of the relaxation function, they enormously overpredicted the relaxation times themselves (and the consequent viscosities) by up to a factor of 10^6. This factor disappears when constraint-release is accounted for self-consistently. It is, however, important to stress that the tube dilation concept is only applicable when the star arms are well entangled. For arm lengths of molecular weight less than M_e, the viscosity of a melt of star polymers is actually *less* than that of the linear polymer of equal molecular weight: without entanglements the star relaxes via Rouse-like modes for which the terminal time is dominated by the longest connected path through the polymer. As in the case of linear polymers, the nature of the dynamics in the presence of weak entanglement is much less well understood than the cases of strong (tube model) or absent (Rouse model) entanglement. The present calculation which admits a time-scale-dependent entanglement density can be expected to perform as well as it does for pure star melts at very long and short times (when these limits apply) but for the same reason will not define the cross-over between entangled and non-entangled dynamics.

Tube dilation and constraint-release

It is important to stress that the validity of assuming that the relaxation is governed by a dilated tube is correct only because of the very slow chain dynamics of branched polymers. It might be thought that the picture is equally correct for a bimodal blend of two linear polymers, when the slow dynamics of the long chains exist in dilated tubes such that the short chains constitute effective solvent. However, Viovy, Rubinstein and Colby have shown that this is not always the case[7,8,10]. By ascribing Rouse-like dynamics to the tube itself and allowing the tube of short-lifetime constraints to reptate within the larger tube of long-lifetime constraints, they find a regime of behaviour which mimics a tube-dilation approach with a renormalized friction constant (a regime they term 'tube reptation') only under an additional constraint on the molecular weight of the short chains M_s that $(M_s/M_e)^3 < 1/\phi$ where ϕ is the volume fraction of long chains. The physical effect underlying this constraint is that outside it a *faster* relaxation process is available to the long chains: namely reptation within their immediate tubes. It is conjectured that such a regime does not exist for branched polymers because in this case relaxation in a dilated tube is exponentially faster while friction constants still renormalize as a power law of length-scale. This will be discussed in greater detail elsewhere.

STAR-LINEAR BLENDS

In this paper we concern ourselves with the problem of stress-relaxation in a melt containing just two fractions: a linear flexible polymer of molecular weight M_L and a star-branched homopolymer whose arms are of molecular weight M_a. If we denote the volume fraction of the star polymer by ϕ, the volume fraction of the linear polymer becomes $(1-\phi)$. This very simple system still has three effective parameters $\{M_L/M_e, M_a/M_e, \phi\}$ and is the simplest branched analogue of the much-studied bimodal linear blend[6–10]. At this level we make the additional assumption of compatibility between the linear and branched polymers. This is justified in the case of homopolymers from the observed miscibility of branched and linear polystyrenes[1] and, in the case of less well controlled polymerization, the blending of high- and low-density polyethylene without segregation[17]. The assumption of compatibility is an important simplification because it permits the use of a unique mean-field for the topological constraints on both species. It will generally break down in the case of heterogeneous systems in which the species have distinct chemistries or in the important case of star polymers with arms of differing chemistries. This theory is therefore applicable to the technology of rheological modification in homopolymers, but not to the task of compatibilization of blends. In the latter case, an explicit account of the microstructure is required.

Three main cases exist depending on whether the star polymers are entangled among themselves or not $(C_s >< \beta C^*)$ and on whether the terminal time of the star-arm relaxation T_s is longer or shorter than the reptation time of the linear fraction $(T_{rep} >< T_s)$. Experiment indicates that in order to be entangled overlap must be high, not simply of order one, hence the factor β which is large in melts. The criterion on the concentration determines the nature of the long-time dynamics: whether entanglement is effective or not. The second criterion determines which fraction of the melt is responsible for the long-time behaviour. Of course when all polymers are well entangled the molecular weight of the linear fraction must be very high in order to ensure that it is the last to relax, but in principle both limits are accessible. We consider the cases in turn.

Case 1: $C_s >< \beta C^*$; $T_{rep} > T_s$

When the reptation time is long enough then the branched polymers will be constrained by an entanglement network throughout their relaxation. The effective network concentration now contains two contributions from the linear and star fractions, and may be written:

$$C_{net}(t) = \phi \int_0^{M_a} e^{-t/\tau(s)}\, ds + (1-\phi) e^{-t/T_{rep}} \tag{4}$$

As far as the star arms are concerned, the linear fraction is behaving as a fixed network, so using equation (4) in the dynamical equation (1) interpolates between the limits of a star melt treated by Ball and McLeish[13], and the star in a network treated by Pearson and Helfand[4]. Using the step-function approximation for the integrand along the star arm in equation (4) allows us to calculate the set of contour relaxation times $\tau(s)$ by solving equation (1):

$$\tau(s) = \tau_0 \exp \alpha \left[\frac{1}{2}\left(\frac{s}{M}\right)^2 - \frac{\phi}{3}\left(\frac{s}{M}\right)^3 \right] \tag{5}$$

We see that the relaxation times are decreasing functions of the star fraction, reflecting the highly co-operative nature of the constraint-release when branching is prevalent. Varying the star fraction therefore affects both the level of the stress attained when all star polymers have relaxed (as this is carried by the linear chains only) and also the rapidity with which this intermediate plateau is attained. *Figure 2* shows numerical calculations of the quantity $C_{net}(t)$ (recall that $G(t) \sim [C_{net}(t)]^2$) for the case of star polymers such that $\alpha = 20$ $(M_a \approx 5M_e)$ in a matrix of very long linear chains $(M_L \approx 3000 M_e)$. Even in this case of enormously disparate molecular weights, the relaxation time-scales are clearly not widely separated for higher concentrations of the star fraction.

Tube dilation must also affect the linear fraction and the reptation time itself will not be constant as ϕ alone is varied. The effect of diluting the entanglement network seen by the linear chains is to shorten the primitive path length L along which they must diffuse to relax their orientation. Since $T_{rep} \sim L^3$ and $L = (M_L/M_e)a$, the concentration dependence of T_{rep} is predicted to be linear. This is in accord with the findings for the 'tube reptation' regime of Viovy[7]. The shorter reptation times resulting from a more dilute linear matrix are clear from the long-time behaviour of the relaxation curves in *Figure 2*. The condition on the reptation time that the relaxation at long times be reptation of the linear chains therefore implies a joint condition on ϕ and M_L such that $(M_L/M_e) > 1/(1-\phi)$.

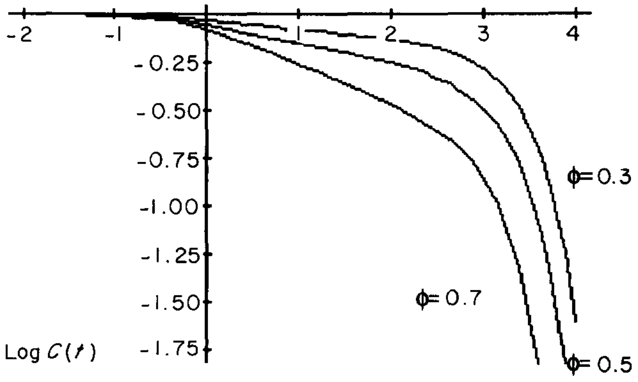

Figure 2 Network relaxation for case 1 when $\alpha = 20$ and $T_{rep}/\tau_0 = e^8$ and three values of ϕ

Case 2: $C_s > \beta C^*$; $T_{rep} < T_s$

This is a more realistic regime than the previous case because the molecular weight of the linear fraction is not as high as the previous case would demand when the star chains are well entangled. The relaxation of the star arms is still always entangled so that $(M_a/M_e) > 1/\phi$, but occurs in two stages. Initially the linear chains contribute to the entanglement network and the arm fluctuation is retarded relative to the case of pure star polymer (we still imagine that $M_L \gg M_a$ so that the fluctuating dynamics of the star arms is faster than that of the linear chains). Then on some intermediate time-scale, when a significant portion of the star arms has relaxed, the linear chains relax via reptation. Following this, the arms continue to relax via breathing, but are now accelerated by the dilated effective tubes. A log–log plot of the stress relaxation will show two regions characterized by the logarithmic decay typical of entangled branched polymers separated by a relatively rapid step, since at the level of this treatment, the reptation time behaves like a single characteristic time-scale for all the segments of the linear chains. Indeed for increasingly large α, the approximation by which we take the contribution of the linear chains to the effective network to decay as a step function becomes increasingly accurate, and is useful because it allows explicit calculation of the relaxation times as in case 1. The dynamical equation becomes:

$$\frac{\mathrm{d}\tau(s)}{\mathrm{d}s} = \tau(s)\alpha\left(\frac{s}{M_a}\right)\left\{\phi\left(1-\frac{s}{M}\right)+(1-\phi)\theta[T_{rep}-\tau(s)]\right\} \quad (6)$$

where $\theta(t)$ is the Heaviside step function. The solution is expressed more simply in terms of an intermediate parameter, s_{rep}, which we define as the contour label of the monomer on the star arm whose relaxation time coincides with the reptation time of the linear chain. The solution for the relaxation times then becomes:

$$\tau(s) = \begin{cases} \tau_0 \exp \alpha\left[\frac{1}{2}\left(\frac{s}{M}\right)^2 - \frac{\phi}{3}\left(\frac{s}{M}\right)^3\right] & s < s_{rep} \\ \tau_0 \exp \alpha\left[\frac{\phi}{2}\left(\frac{s}{M}\right)^2 - \frac{\phi}{3}\left(\frac{s}{M}\right)^3 + \frac{1}{2}(1-\phi)\left(\frac{s_{rep}}{M}\right)^2\right] & s > s_{rep} \end{cases} \quad (7)$$

where the matching condition of continuity of the function $\tau(s)$ supplies the boundary condition for the second region. There is an interesting feature of this regime apart from the unusual relaxation function in that the terminal time $\tau(M)$, and hence the viscosity, may be either an increasing or decreasing function of the star fraction, depending on the value of s_{rep}. (Explicit expressions for the terminal times are given in *Table 1*.) When the linear chains act for long enough as an effective matrix $\tau(M)$ decreases with ϕ, the transition occurring at $s_{rep} = M/3$.

In *Figure 3* we show numerical results for a well entangled star of $(M/M_e) \approx 20$ in the presence of a faster fraction of linear chains. In the case illustrated we have kept s_{rep} constant, though in practice both s_{rep} and T_{rep} are weak functions of ϕ if molecular weights are kept constant. This is due to the mild renormalization of T_{rep} as the effective contribution of the star arms to the entanglement network changes. Both T_{rep} and s_{rep} may be found as functions of the bare (monodisperse melt) value of the reptation time, T_{rep0}, by demanding the self-consistent condition:

$$T_{rep} = T_{rep0}\left(1 - \phi\frac{s_{rep}}{M}\right) = \tau(s_{rep}) \quad (8)$$

Ignoring the renormalization of T_{rep} still demands a cubic be solved for s_{rep} but the solution has a useful expansion in inverse powers of the large parameter α which we quote:

$$\left(\frac{s_{rep}}{M}\right)^2 \approx \frac{2}{\alpha}\ln\left(\frac{T_{rep0}}{\tau_0}\right) + \frac{2\phi}{\alpha^{3/2}}\left\{\left[2\ln\left(\frac{T_{rep0}}{\tau_0}\right)\right]^{3/2} - \left[2\ln\left(\frac{T_{rep0}}{\tau_0}\right)\right]^{1/2}\right\} + \cdots \quad (9)$$

In most relevant cases the reptation time will be significantly shorter than the terminal time for the star arms in which case this expansion is adequate. There are two contributions to the second term in equation (9) because the effects of renormalization of T_{rep} and the cubic correction to log $\tau(s)$ enter at the same order of α. The renormalization of T_{rep} itself has a similar expansion in inverse powers of α, and in this regime works to prolong the relaxation of the linear chains as the fraction of branched material is increased.

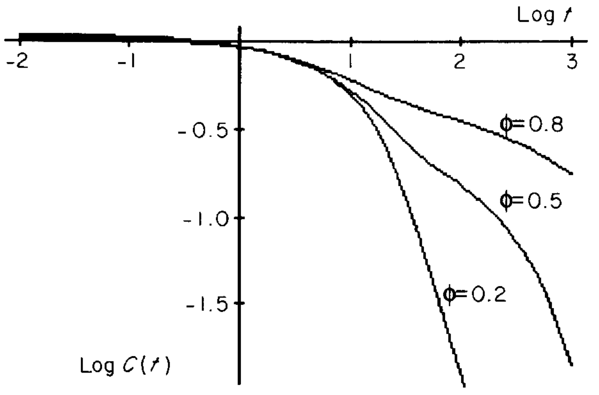

Figure 3 Network relaxation for case 2 when $\alpha = 60$ and $s_{rep} = 0.3$ and three values of ϕ

Table 1 Dependence of the terminal relaxation times on molecular weights of the star and linear fractions for each case referred to in the text. The parameter s_{rep} is dependent on the molecular weights via equation (9)

	$C_s < C^*$		$C_s > C^*$
$T_{rep} > T_s$	$\tau \exp\left[\frac{\nu M}{M_e}\left(1-\frac{2C_s}{3}\right)\right]$		$\tau \exp\left[\frac{\nu M}{M_e}\left(1-\frac{2C_s}{3}\right)\right]$
	$\frac{M}{M_e} < N_e^4$	$T_{rep}\left(\frac{M}{M_e}\right)^2$	
$T_{rep} < T_s$	$\frac{M}{M_e} > N_e^4$	$T_{rep}\left(\frac{M}{M_e}\right)^{3/2} N_e^2$	$\tau \exp\left\{2\frac{\nu M}{M_e}\left[(1-C_s)\frac{s_r^2}{2}+\frac{M^2 C_s}{6}\right]\right\}$

Case 3: $C_s < \beta C^*$; $T_{rep} < T_s$

This case is the only remaining distinct one as the overlap or non-overlap of the star fraction is only effective when the linear fraction is effectively solvent at long times. The initial relaxation of the star polymers proceeds via entangled path fluctuation from the free ends as before, but at long times the stars are effectively dilute so must relax via Rouse modes with an effective local friction provided by the viscoelastic linear matrix. The novel feature of such a Rouse relaxation however is that the initial condition on the orientational distribution of the star arms (which is imposed at T_{rep} when free relaxation can begin) is such that no stress is carried by segments such that $s < s_{\mathrm{rep}}$. If we approximate the modes on the star polymer by linear Rouse modes:

$$X_p = \frac{1}{N}\int_0^N \cos\left(\frac{p\pi s}{N}\right)\boldsymbol{R}(s)\,\mathrm{d}s \qquad (10)$$

we may find their initial amplitudes X_p from the condition that segments are affinely deformed with the shear up to $s < s_{\mathrm{rep}}$:

$$\begin{cases} R_x(s) = R_x(s)|_{\mathrm{eq}} + \gamma R_y(s)|_{\mathrm{eq}} \\ R_y(s) = R_y(s)|_{\mathrm{eq}} \end{cases} \qquad (11)$$

Here γ is the magnitude of the shear, which is taken to be in the x–y plane. The magnitude of the shear stress under a step shear strain is easily calculated as a sum over these modes, which decay independently and exponentially:

$$\sigma_{xy}(t) \propto \sum_p p^2 \langle X_{px}(t) X_{py}(t)\rangle \qquad (12)$$

and

$$\frac{\partial}{\partial t}\langle X_{px}(t)X_{py}(t)\rangle = -\frac{p^2}{T_{\mathrm{Rouse}}}\langle X_{px}(t)X_{py}(t)\rangle$$

The initial mode amplitudes determine the form of the relaxation spectrum. These are calculated from equations (10) and (11) in terms of equilibrium chain conformations:

$$\langle X_{px}(0)X_{py}(0)\rangle = \frac{1}{N^2}\int_0^N \mathrm{d}s \int_0^{N-s_{\mathrm{rep}}} \mathrm{d}s' \left(\frac{N}{p\pi}\right)^2 \left\langle \frac{\partial R_y(s)}{\partial s}\frac{\partial R_y(s')}{\partial s'}\right\rangle \times \sin\left(\frac{p\pi s}{N}\right)\sin\left(\frac{p\pi s'}{N}\right) \qquad (13)$$

The angular brackets denote an equilibrium average. In this case the averaged quantity is the second moment of the local chain extension. It is directly evaluated from the Wiener measure for configurations of Gaussian chains[5] as $b^2/3\ \delta(s-s')$, where b is the Kuhn step length, thus allowing direct integration of equation (13) to find:

$$\langle X_{px}(0)X_{py}(0)\rangle = \frac{b^2}{6p^2\pi^2}\left[(N - s_{\mathrm{rep}}) - \frac{N}{2p\pi}\sin\frac{2p\pi(N - s_{\mathrm{rep}})}{N}\right] \qquad (14)$$

We observe straight away that for small s_{rep} we recover the familiar $1/p^2$ amplitudes for the Rouse decay. However, for $s_{\mathrm{rep}} \rightarrow N$ (the case in which most of the stress has decayed by path-length fluctuation before free Rouse motion can begin) we find that all modes have approximately the same amplitude of $2b^2(N - s_{\mathrm{rep}})^3/N^2$ up to the mode characterizing the length of stressed primitive path $[p \approx N/(N - s_{\mathrm{rep}})]$. This is easy to understand for the short portion of stressed path length approximates to a delta function on these length-scales and the mode amplitudes will follow the form of the Fourier transform of a delta function, which is constant in mode index. Slower modes are more heavily weighted than in the standard case. The effect of this is to alter the power-law decay of the stress which one obtains from summing the Rouse modes[5] from $t^{-1/2}$ to $t^{-3/2}$ for the initial stages of the free relaxation. This is easily seen from writing an integral approximation to the expression for the stress decay in equation (12):

$$\sigma_{xy}(t) \sim \int_0^{\infty} p^2 \mathrm{e}^{-p^2 t}\,\mathrm{d}t \sim t^{-3/2}\int_0^{\infty} z^2 \mathrm{e}^{-z^2}\,\mathrm{d}z \qquad (15)$$

We note that the experiments of Watenabe *et al.*[1] on polystyrene blends fall into this class and that their frequency-dependent moduli at low frequency do indeed show a power-law form between the reptation times of the linear polymer and the terminal time of the star fraction which is consistent with this result. We show in *Figure 4* some of the data of Watenabe *et al.*, this time in the frequency domain together with the theory for the terminal zone alone for $(N - s_{\mathrm{rep}})/N = 0.1$. The fraction of star polymer was 1/60, the molecular weight of the linear component 315 000 and the star-arm molecular weight 400 000.

A final, distinctly different regime exists within the case of self-dilute stars when the star-arm molecular weight is so long that hydrodynamic ('Zimm') relaxation is faster than the Rouse-like relaxation discussed above. This must occur since the Zimm time increases as $M_{\mathrm{a}}^{3/2}$ while the Rouse time grows as M_{a}^2. The cross-over molecular weight can be estimated by equating the two times under the following assumptions:

1. The Rouse time for a segment of molecular weight M_{e} in the melt is τ.
2. The renormalized Rouse time for the star arm is $(M_{\mathrm{a}}/M_{\mathrm{e}})^2\tau(M_{\mathrm{L}}/M_{\mathrm{e}})^3$. This is equivalent to giving an elemental Rouse hopping time to the tube equal to the reptation time of the linear chains.
3. The renormalized Zimm time of the star arm is the time it takes to diffuse hydrodynamically through its own radius of gyration $\sim R_{\mathrm{a}}^3\eta/kT$ with the viscosity $\eta \sim kTv(M_{\mathrm{L}}/M_{\mathrm{e}})\tau(M_{\mathrm{L}}/M_{\mathrm{e}})^3$. Here v is the number

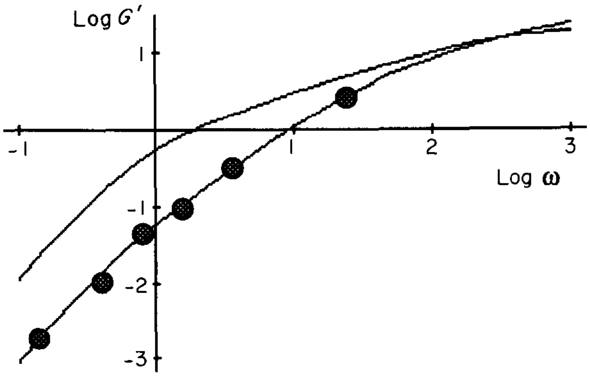

Figure 4 $G'(\omega)$ for a star-linear blend of case 3. Data of Watenabe *et al.* (●) compared to free-Rouse (upper curve) and our predictions of 'anomalous Rouse' (lower curve). We have taken $s_{\mathrm{rep}}/M = 0.9$ and fitted the terminal zone of the linear component so that only the low-frequency star-dominated response remains. To the left of the G' axis the slope is 2 (final relaxation); to the right it is 3/2 (anomalous Rouse relaxation) for a decade of frequency before approaching a plateau

density of chains so that $kT\nu(M_L/M_e)$ is an estimate of the plateau modulus of the melt.

These assumptions together imply that if $N_a > N_e^2$ then the final relaxation occurs hydrodynamically. We note that this is also the criterion that solvent chains of molecular weight M_e screen the long star arms effectively from their own excluded-volume interactions. Longer star arms will tend to swell.

DISCUSSION AND CONCLUSIONS

We may conclude from the above that the system comprising a homopolymer blend of linear and star polymers is amenable to a tube-dilation analysis when both components are well entangled. Novel rheological behaviour emerges even at the level of linear response as different regions of the molecular weight/concentration phase diagram are explored. An illustration of the variety of behaviour is shown in *Table 1*, which gives the characteristic terminal times for relaxation of the star fraction as a function of molecular weight and volume fraction of star polymer. This summarizes the discussion above.

A related question of relevance to applications of this system is the effect of polydispersity. Of course the star-linear blend itself is an example of strong polydispersity of *relaxation times*. Such strong polydispersity can also be generated in the case of linear melts if the molecular weight range is very large indeed. When reptation times in such a blend vary over decades the tube-dilation concept can be invoked, as shown recently for weak power-law polydispersity[18]. In this limit it is straightforward to see that the modification of the present approach to include polydispersity would replace the network of the monodisperse linear chains fixed for $t < T_{rep}$ with a dilating tube corresponding to the low molecular weight fractions of linear polymer. This will accelerate the relaxation of the branched component over the monodisperse case and remove sharp features from the relaxation spectrum, such as the step at the terminal time of the linear fraction. Conversely the presence of a high molecular weight tail provides a weak but long-lived contribution to the modulus for which entanglements are not important providing that the tube dilates fast enough. It turns out[18] that the condition for this is that the high molecular weight tail for the distribution has a distribution $P(M)$ which falls away more rapidly than M^{-2}. In the case of longer tails to the distribution the persistence of effective entanglements for both linear and branched species may lead to relaxation times well beyond those usually measured in the laboratory.

Experiments on well characterized branched/linear blends are still lacking in most of the regimes of interest, though should be possible in the near future. The case of self-dilute stars is so far in agreement with theory. Of particular interest is case 2 in which all the phenomena of reptation, accelerated relaxation of star arms and a terminal unrelaxed phase are expected. These should be clear from the linear stress-relaxation spectrum. For this case the star and linear fractions should be roughly equally admixed. This case is also a useful tool for studying the intermediate dynamics of weakly entangled polymers. Rheological experiments on polymers with lower entanglement molecular weight, so further into the entangled regime, such as polyisoprenes, would also be welcomed. Extensions of this work would apply to blends of more complex branched architectures in linear melts. Molecules with more than one branch point per molecule have markedly different non-linear rheology from that of non-branched or singly branched molecules, and might be effective as rheological modifiers.

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