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# Dynamic Dilution and the Viscosity of Star Polymer Melts

**R. C. Ball and T. C. B. McLeish***

*Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.*

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ABSTRACT: We apply a method of treating constraint release in the dynamics of branched polymers to an outstanding problem in the viscosity of star polymer melts. In the approximation of complete separation of time scales along a star arm, it is shown that cooperative effects dilute the effective entanglement by a factor 3, giving much improved quantitative agreement with rheological experiments. Polydispersity is found to affect the terminal time and viscosity only via the weight-average molecular weight.

## Introduction

Alongside the application of the tube model to linear polymer melts,[1] it was realized that it could also predict the long-time dynamical behavior of star polymers.[2,3] In this case, loss of orientation of the entangled chain segments occurs via the "breathing modes" of the arms, and the total stress after a step strain is proportional to the length of tube still unvisited by a chain end, as for linear chains. The full relaxation spectrum was calculated by Pearson and Helfand,[4] and the resulting viscosity has a dependence on the molecular weight of the arms, $M$, given by

$$\eta_0 \sim M^{1/2} \exp\{\nu M/M_e\} \tag{1}$$

where $M_e$ is the entanglement molecular weight. The tube model gives a prediction for the dimensionless number $\nu$ of 15/8.[5] However, although experiments confirm the dominant exponential form of (1),[4] a value for $\nu$ of around 0.6 is found. This is also seen in the molecular weight dependence of the diffusion constant.[6] Over even a narrow range of molecular weights, this gives enormous discrepancies in the viscosity and demands an explanation. There are also small discrepancies in the form of the relaxation modulus even when $\nu$ is fitted by experiment.[4] The fundamental cause is conjectured to be that of "constraint release" whereby loss of orientation in chain segments is permitted by the diffusion of neighboring chains. This is evident in the relaxation of linear melts,[7,8] especially when polydispersity is important, and is bound to be more significant in branched polymers, which have a much broader range of relaxation times among molecular segments. A low value of $\nu$ also corresponds to a high apparent value of $M_e$ which can be thought of as a dilated tube, an idea which motivates one approach to constraint release.

The dilated tube concept was applied to linear polymers by Marrucci.[9] In this picture, constraint release speeds up reptation because relaxed parts of the chains are taken to dilute the effective entanglement network of the still unrelaxed chain, effectively shortening the remaining primitive path length. The validity of this approach in the case of linear chains is questionable, however, for although chain ends do relax faster than chain centers the two time scales are not widely separated (both scaling as the reptation time) as is necessary for a true solvent action.

The expression for the stress as a function of unrelaxed path length is another important issue in the dilated tube theory. Marrucci[9] suggests a departure from mutual proportionality. Indeed, if relaxed path length really acts as a solvent for the remainder, then the stress should fall as the *square* of the unrelaxed path length. This is the experimental dependence of the plateau modulus $G_0$ of entangled polymer solutions with concentration $c$:

$$G_0 \sim c^2 \tag{2}$$

so

$$G(t) \sim [F(t)]^2 \tag{3}$$

where $F(t)$ is the fraction of unrelaxed path length at time $t$ after a step strain. A more appropriate case for this "dynamic dilution" limiting form of constraint release is found in branched polymers where the separation of relaxation time scales of different parts of the entangled molecule is much wider than in linear polymers.[4] The idea has been applied successfully to entangled H polymers[10] and speculatively to tree polymers.[11] In this paper we calculate how the stress relaxation of star arms is modified in this limit.

## Dynamic Dilution of a Relaxing Arm

In the calculation of the stress relaxation of a star arm by fluctuation of its free end, a quantity of interest is the function $p(s,t)$: the probability that a segment of arc length coordinate $s$, measured inward from the free end, is still unrelaxed at time $t$ ($0 < s < M$, the molecular weight of a single arm). In the limit of long arms, this function approaches a step function in $s$ for all times between the Rouse time for an entanglement length and the time scale for complete relaxation of an arm.[4] In this limiting case, each part of the arm has a well-defined relaxation time $t(s)$, and we can greatly simplify the analysis by writing an approximate ordinary differential equation for $t(s)$ rather than consider the full Smoluchowski equation for $p(s,t)$.

We first present the undiluted case appropriate to relaxation of an arm in a permanent net. The differential equation can be derived by considering the relaxation of the primitive path from $s$ to $s + ds$ as an activated process with an attempt frequency of $[t(s)]^{-1}$ so that

$$t(s + ds) = t(s)e^{dU/kT} \tag{4}$$

where $U$ is the path length free energy potential which may be written[5] as

$$U(s) = \frac{kT\nu}{M_e M}\{(M - s)^2 - 2M(M - s)\} \tag{5a}$$

$$U(s) = \frac{kT\nu s^2}{M_e M} + \text{constant} \tag{5b}$$

This comes from two entropic terms: the rubber elastic potential for the end-to-end distance of a chain within a tube (the quadratic term in (5a)), and the tension at the chain end due to its free exploration of the entanglement network (the linear term in (5a)).[5] The value for $\nu$ of 15/8 comes from the tube model calculation of the plateau modulus ($G_0$) and the definition of $M_e$ in terms of $G_0$, the polymer density $\rho$, and temperature:

$$M_e = \frac{\rho kT}{G_0} \tag{6}$$

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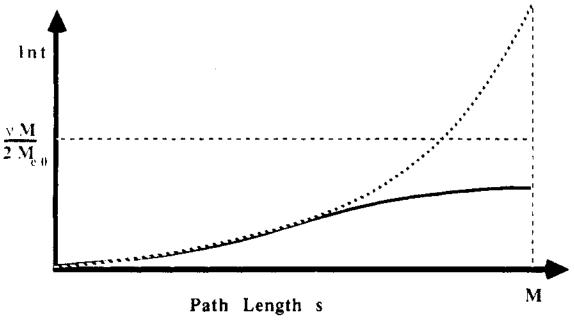

**Figure 1.** Relaxation time of segments of molecular distance *s* from the free end of a star arm, measured along the primitive path. The dashed line corresponds to no constraint release, the continuous curve to the dynamic dilution result.

Substituting (5) into (4) and taking limits $\{ds/M \rightarrow 0; dU/U(M) \rightarrow 0\}$ (on the understanding that this is an intermediate limit maintaining $[t(s + ds)/t(s)] \gg 1$) gives the differential equation

$$\frac{dt}{ds} = \frac{2\nu}{M_e}\left(\frac{s}{M}\right)t(s) \qquad (7)$$

This has the solution

$$t(s) = t_0 \exp\left\{\frac{\nu s^2}{M_e M}\right\} \qquad (8)$$

Here $t_0$ is the Rouse time for an entanglement length, the time beyond which chain dynamics are governed by entanglements. The exponential factor in the viscosity comes from the terminal time $t(M)$,

$$t(M) = t_0 \exp\left\{\frac{\nu M}{M_e}\right\} \qquad (9)$$

which reproduces the expressions in the literature to within a prefactor.[3,4]

To apply the dynamic dilution hypothesis, we alter eq 7 so that the entanglement molecular weight varies consistently with the relaxation of the chains and the known concentration behavior of the modulus (eq 2):

$$M_e(s) = \left(1 - \frac{s}{M}\right)^{-1} M_{e0} \qquad (10)$$

Here $M_{e0}$ is the undiluted entanglement molecular weight.

The effective increment of potential $dU(s)$ becomes diluted because, although we maintain $s$ $(0 < s < M)$ as a coordinate throughout the relaxation, the actual primitive path length for the arm is reduced at longer time scales. Similarly the effective entropic tension at the chain ends is reduced at longer time scales as the entanglement network is diluted. Now (7) becomes

$$\begin{aligned}\frac{dt}{ds} &= \frac{2\nu}{M_e(s)}\left(\frac{s}{M}\right)t(s)\\ &= \frac{2\nu}{M_{e0}}\left(1 - \frac{s}{M}\right)\left(\frac{s}{M}\right)t(s)\end{aligned} \qquad (11)$$

The solution is still straightforward:

$$t(s) = t_0 \exp\left\{\frac{2\nu}{M_{e0}M}\left(\frac{s^2}{2} - \frac{s^3}{3M}\right)\right\} \qquad (12)$$

Figure 1 compares this solution to the corresponding zero constraint release case. We see that, as well as changing the form of the relaxation, the longest relaxation time of the system, $t(M)$, is now $\exp\{\nu M/3M_{e0}\}$ or that the effective value of $\nu$ has been decreased by a factor 3. This factor carries over to the viscosity via

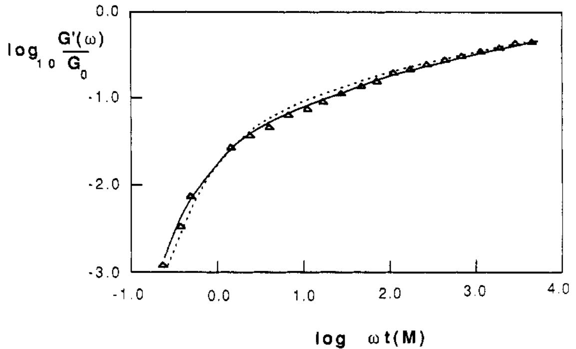

**Figure 2.** Dynamic storage modulus according to experiment and theory. Triangles are results on a polyisoprene from ref 4. Dashed line is the zero constraint release theory with adjusted values of $\nu$ and plateau modulus. Solid line is the present theory with only the terminal time fitted to experiment.

$$\eta_0 = \int_0^\infty G(t)\,dt$$

with

$$G(t) = \frac{2G_0}{M}\int_0^M e^{-t/t(s)}(1 - s/M)\,ds \qquad (13)$$

The last expression for $G(t)$ becomes, in the limit $M/M_{e0} \gg 1$,

$$G(t) = \begin{cases} G_0 & t < t_0 \\ G_0\left[1 - \frac{s(t)}{M}\right]^2 & t_0 > t > t(M) \\ G_0\left(\frac{M_{e0}}{\nu M}\right)\frac{t(M)}{t}\exp\left\{\frac{-t}{t(M)}\right\} & t > t_0 \end{cases} \qquad (14)$$

The form for intermediate times obeys the modulus dilution hypothesis of (3) where $F(t) = [1 - s(t)/M]$. Now the viscosity becomes

$$\eta_0 = G_0\left(\frac{\nu M}{M_{e0}}\right)^{-1} t(M) = G_0\left(\frac{\nu M}{M_{e0}}\right)^{-1} \exp\left\{\frac{\nu M}{3M_{e0}}\right\} \qquad (15)$$

and we see that the effective value of $\nu$ is (1/3) × 15/8 = 0.625, which compares very favorably with the experimental value of 0.6 reported in ref 4.

Another interesting prediction of this model concerns the recoverable complience $J_e^0$, which we calculate according to

$$J_e^0 = \frac{1}{\eta_0^2}\int_0^\infty tG(t)\,dt \qquad (16)$$

The dynamic dilution result using (13) and (16) is that $J_e^0 G_0 = \nu M/2M_{e0}$, which compares with the zero constraint release result[4] of $J_e^0 G_0 = \nu M/M_{e0}$. So if we measure the recoverable compliance, the effective value of $\nu$ is reduced by a factor of 2 rather than the factor of 3 which emerges in the viscosity. Assembled data on the product $J_e^0 G_0$ have been presented as consistent with an effective $\nu$ of 0.6,[4] but the results show a lot more scatter than do measurements of viscosity, and would not be in contradiction with this higher theoretical value of (1/2) × 15/8 = 0.94.

As a final comparison with experiment, we present predictions for the dynamic storage modulus for a star melt with $M/M_e = 20$ in Figure 2. The experimental results (on polyisoprene in this case) and predictions of the zero constraint release model are taken from Figure 5 of ref 4. We see that with no artificial adjustment of $\nu$ or of $G_0$ (which was adjusted by ~5% in ref 4) the dynamic dilution result improves on the (already very good) predictions of the simpler model.

## Polydispersity

It is interesting to explore the effects of polydispersity within the dynamic dilution model, particularly as it is possible that it may also affect the observed value of $\nu$ even for the fairly monodisperse samples used in experiments.[4] The new element in the calculation is an average over the distribution of arm lengths in the expression for the effective entanglement molecular weight:

$$M_e(t) = \left\{ \int_{M_r}^{\infty} \left[ 1 - \frac{s(t,M)}{M} \right] \phi(M)\, \mathrm{d}M \right\}^{-1} M_{e0} \quad (17)$$

Here $M_r$ is the molecular weight of arms which have just relaxed at time $t$. The density distribution by weight of polymers of molecular weight $M$ is $\phi(M)\,\mathrm{d}M$, where the function $\phi(M)$ is normalized. One delicate point is that the amount of relaxed arm length after a time $t$, $s(t)$, is not independent of the arm molecular weight. Long arms have softer quadratic elastic potentials, so initially lose entangled path length faster than in short arms. This makes it impossible to write down a unique equation for $s(t)$ analogously to (7). However, the simple form is regained if we work in terms of the largest potential explored by a chain end by time $t$, $U(t)$, rather than $s(t)$. This is because $U(t)$ is universal among all molecular weights (except those which are completely relaxed) as can be seen from the basic dynamical equation (4). We may then calculate $s(U,M)$ by inverting (5). Thus,

$$\frac{\mathrm{d} \ln t}{\mathrm{d}U} = \frac{1}{kT}\left( \frac{M_{e0}}{M_e(t)} \right) \quad (18)$$

giving

$$\ln (t/t_0) = \int_0^U \mathrm{d}U' \frac{1}{kT} \int_{M_r}^{\infty} \left[ 1 - \frac{s(U',M)}{M} \right] \phi(M)\, \mathrm{d}M \quad (19)$$

Now substituting for $s(U,M)$ and $M_r(U)$ from (5), we find that $t(U)$ is given by the double integral

$$\ln \left( \frac{t}{t_0} \right) = \int_0^U \mathrm{d}U' \frac{1}{kT} \int_{U'M_e/\nu kT}^{\infty} \left\{ 1 - \left( \frac{M_e U'}{kTM\nu} \right)^{1/2} \right\} \phi(M)\, \mathrm{d}M \quad (20)$$

This is straightforward to evaluate, and the longest relaxation time is given by the limit as $U \rightarrow \infty$ (the point at which the tail of the distribution relaxes). This is the quantity of main interest as we have seen because it is the principal contribution to the large viscosity of star melts. The result is

$$t_{\max} = t_0 \exp\left\{ \frac{\nu}{3M_{e0}} \int_0^{\infty} M\phi(M)\, \mathrm{d}M \right\} = t_0 \exp\left\{ \frac{\nu M_w}{3M_{e0}} \right\} \quad (21)$$

So the terminal time $t_{\max}$ (which becomes $t(M)$ in a monodisperse sample) is affected by polydispersity only through the weight-average arm molecular weight, $M_w$. The *prefactor* to this exponential term in the expression for the viscosity will vary with the distribution because it respresents the effective modulus at the terminal time, and this is dominated by the tail of the distribution. However, this effect is dwarfed by the exponential term for small polydispersity, so we have the interesting result that for the viscosity of star polymer melts mild polydispersity is correctly accounted for by working in terms of the weight-average molecular weight.

## Conclusions

The dynamic dilution approach to constraint release becomes applicable to star polymers in the limit of long arms without some of the difficulties associated with theories of constraint release in linear polymers. It can explain the outstanding discrepancies in viscosity, recoverable compliance, and relaxation modulus of star polymer melts. More experiments on the molecular weight dependence of the recoverable compliance would help to confirm or refute the prediction that the prefactor should differ from that of the dependence of log (viscosity).

Experiments on well-defined but polydisperse stars (binary blends for example) would test the prediction that the terminal time depends only on the weight-average molecular weight.

We also note that in this work we have assumed that the branch points of star molecules are fixed during stress relaxation. This will hold good for high functionalities when the arm molecular weight of a *given* star are equal but may have to be modified in other cases.

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