PII: S0032-3861(97)10021-0

Polymer Vol. 39 No. 16, pp. 3877–3881, 1998

0032-3861/98/$19.00+0.00

The blend rheology of some linear and branched polymers

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(Received 10 July 1997; accepted 24 September 1997)

The first stage of a study of model blends using essentially monodisperse linear and three-arm-star polystyrenes is described in relation to the structure-specific blending rule of McLeish and O'Connor and the more general blending law of Tsenoglou for the relaxation shear modulus G(t). The results are considered in relation to the polymer molecular weights, consequent level of entanglement and the effect of cooperative relaxation in the choice of blending rule theory and quality of fit to the data. It is anticipated that the complete study with a range of linear and star polystyrenes will aid the understanding of more general linear–branched polymer blend systems. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: blend rheology; linear polymers; branched polymers)

Introduction

The rheology of blends of linear polymers with long-chain branched polymers has received much less attention than linear–linear polymer blends. To further our understanding of the linear–branched blends we are also studying well characterized, structure-specific, blends of linear and star polymers in order to establish the contribution of the molecular mechanisms in controlling mutual relaxation of blends.

Although the addition rule of Tsenoglou[1–3] works well enough with linear–linear blends, it is not clear that it should be applicable to blends of linear and branched polymers, because the molecular dynamics responsible for stress–relaxation in the two cases are very different. Whereas the linear polymer is free to reptate or relax by motion of the entire chain[4], the motion of the branched polymer will be constrained by the branch points and limited to progressive retractions[5–7]. However, we have found that an empirical extension of the Tsenoglou blending rule can give a satisfactory representation of the rheology of some linear–branched polyethylene blends using polydisperse commercial polymers[8]. In order to understand the mechanisms involved, we are studying some idealized model blends of monodisperse linear and star-shaped polymers, which might be expected to conform more closely to the specific star–linear blending rule of McLeish and O'Connor[6], allowing us to compare the application and limitation of the two blending rules. Earlier work on a similar system by Struglinski *et al.*[9] showed in particular that relaxation time scales change on blending branched with linear materials.

The work reported here represents the first step in the study of a range of star–linear blends intended to cover a range of polymer molecular weights, particularly of the linear in relation to the star polymer. Initially blends of an essentially monodisperse three-arm polystyrene star polymer with linear polymer equivalent to one arm of the star were manufactured within the Polymer IRC at the University of Bradford.

Equations from theory

The basic blending rules used here are given in refs [1–3]. The empirical extension of the Tsenoglou theory[7] takes the generalized form for G(t):

$$\mathrm{G}(t) = (\phi_1 \mathrm{G}_1^{1/a}(t) + \phi_2 \mathrm{G}_2^{1/a}(t))^a \tag{1}$$

where a is blend dependent and can be determined from the zero shear viscosities of the component polymers. ϕ_1 and ϕ_2 are the blend fractions.

In the original form of the equation for linear polymer blends[1–3], $a = 2$, but in the case of blends with branched polymers, e.g. for linear with branched polyethylene[7]:

$$a = A\left(\frac{\eta_{0B}}{\eta_{0L}}\right) + B$$

where $a < 2$ or $a > 2$ depending on the blend components, η_{0B} and η_{0L} are the zero shear viscosities of the branched and linear polymers respectively, and A and B are constants.

In the case of blends using monodisperse 'model' star and linear polymers, the specific molecular theory of McLeish and O'Connor, based on a tube model for entangled polymer melts, takes the form:

$$\mathrm{G}(t) = \left(\phi_1 \mathrm{G}_1^{1/b}(t) \int_0^1 \mathrm{e}^{-t/\tau(X)}\mathrm{d}X + \phi_2 \mathrm{G}_2^{1/b}(t)\mathrm{e}^{-t/T_{rep}}\right)^b \tag{2}$$

where dX is an element at distance X along a star arm, T_{rep} is the reptation time of the linear polymer, and it is assumed *via* G_1 and G_2 that the value of G_o for the linear and star polymers may differ in practice.

The theory allows for cooperative relaxation of the star and linear components with:

$$\tau(X) = \tau_0 2\alpha\left[\frac{X^2}{2} - \phi_1\frac{X^3}{3}\right] \tag{3a}$$

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for $X < X_{rep}$, where $\alpha = \frac{15}{8}\left(\frac{M_a}{M_e}\right)$ and

$$\tau(X) = \tau_0 2\alpha \left[\phi_1 \frac{X^2}{2} - \phi_1 \frac{X^3}{3} + \phi_2 \frac{X_{rep}^2}{2}\right] \tag{3b}$$

for $X > X_{rep}$. Here X_{rep} is the coordinate of the star arm just unrelaxed at the reptation time of the linear polymer. The relaxation of the linear polymer speeds up that of the remaining star polymer by 'constraint release', modelled in this approach by a widening of the effective tube surrounding the star polymer arms. In the case of a linear polymer of lower molecular weight, which may relax quickly by reptation relative to the relaxation of a star arm, a simpler form of equation with less cooperative behaviour may be appropriate, as:

$$\tau(X) = \tau_0 2\alpha \left[\frac{X^2}{2} - \frac{X^3}{3}\right] \tag{4}$$

The various forms of these chosen models are investigated according to known structure of the blend using experimental data.

Experimental

Polymers. Essentially monodisperse polystyrene polymers were made in the form of three-arm star polymers with arms of essentially equal length. Residual linear polymer was removed by solvent fractionation. Linear polymer was subsequently added back to produce blends from solution. For the blend reported here the linear polystyrene had a molecular weight of approximately 78 000, which was the same as one star-arm, i.e. the star polymer molecular weight was approximately 234 000. Blends of 0, 25, 50, 75 and 100% star polymer were produced.

Samples were prepared for rheology from a powder or fluff by cold pressing to form discs of just over 1 mm thick. These were vacuum dried at 80°C to remove any residual moisture and solvent.

Measurement. All measurements were made using a Rheometrics Dynamic Analyser (RDA2) at various temperatures in a nitrogen atmosphere, with all data referenced to 160°C. A torsional transducer range of 0.2–200 gm cm was used with a 10 mm diameter 5° cone and plate geometry. This allows the measurements to be made with less than 50 mg of polymer. The time dependence of the relaxation modulus G(t) from an angular step shear strain and the frequency response of the dynamic moduli G' and G'' were both determined in a linear viscoelastic response range of strain independent data.

Results

Measurements of G' and G'' as functions of angular frequency and G(t) as a function of time, t, made at appropriate temperatures, were shifted by time–temperature superposition to 160°C, covering the ranges of from 10^{-2} to over 10^4 rad s^{-1} for G' and G'', and t from 10^{-3} to almost 10^2 s for G(t).

Due probably to the molecular weight of 78 000 per star-arm and for the linear polymer, which is only four entanglements for polystyrene, the frequency dependence of G', G'', shown in *Figures 1 and 2* for the linear and star polymers respectively, does not follow an ideal classic form, to determine values of τ_0, T_{rep} and G_0, for example. We have therefore used the additional check of best theoretical fit to the G(t) data for the star and linear blend components to confirm appropriate values for these parameters. Although theory tends to assume a single G_0 for a polymer type, we have found that these linear and star polystyrenes have

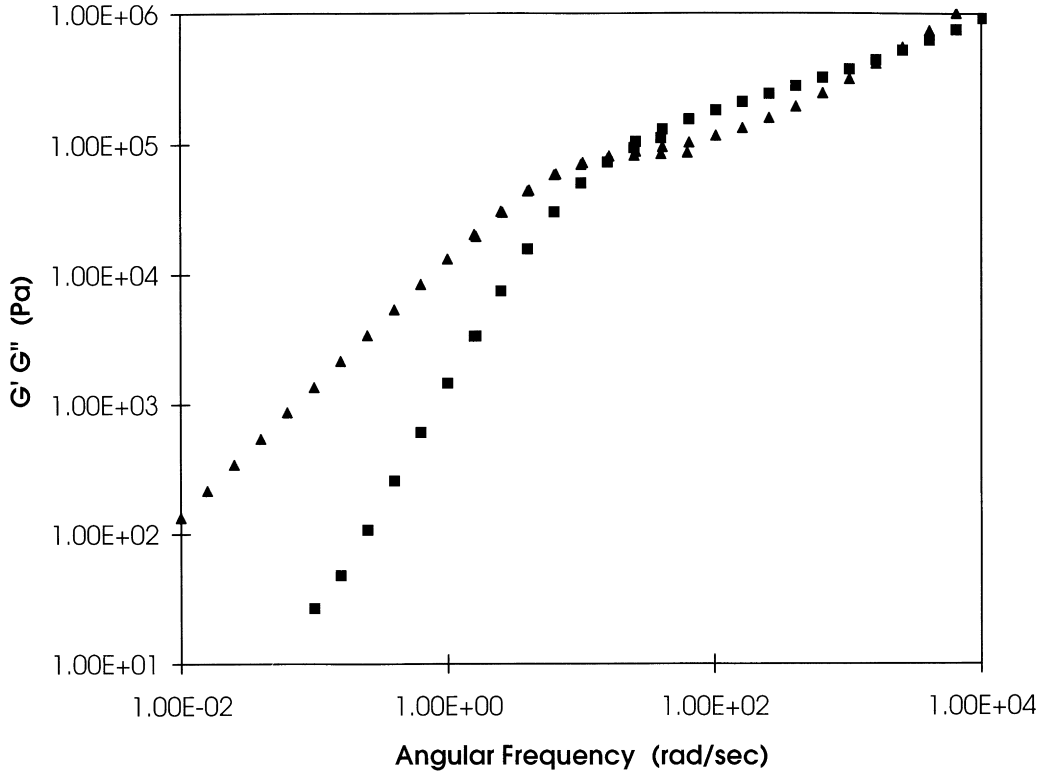

Figure 1 Dynamic shear moduli of the linear polystyrene: elastic modulus G', ■; loss modulus G'', ▲

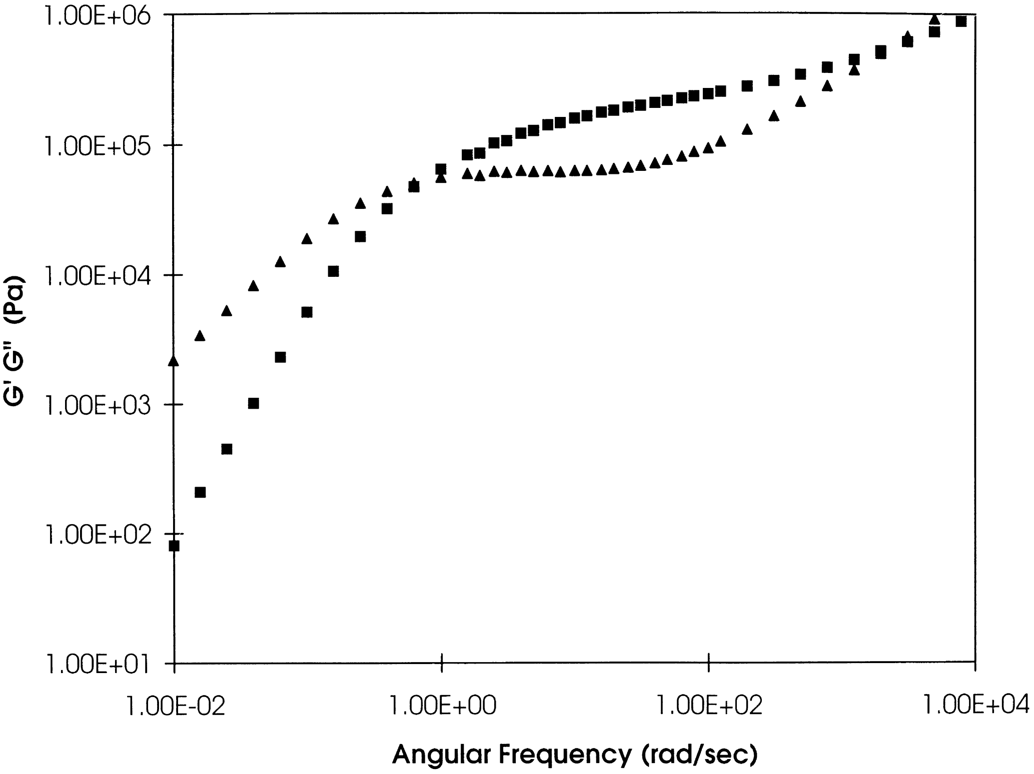

Figure 2 Dynamic shear moduli of the three-Arm star polystyrene: elastic modulus G', ■; loss modulus G'', ▲

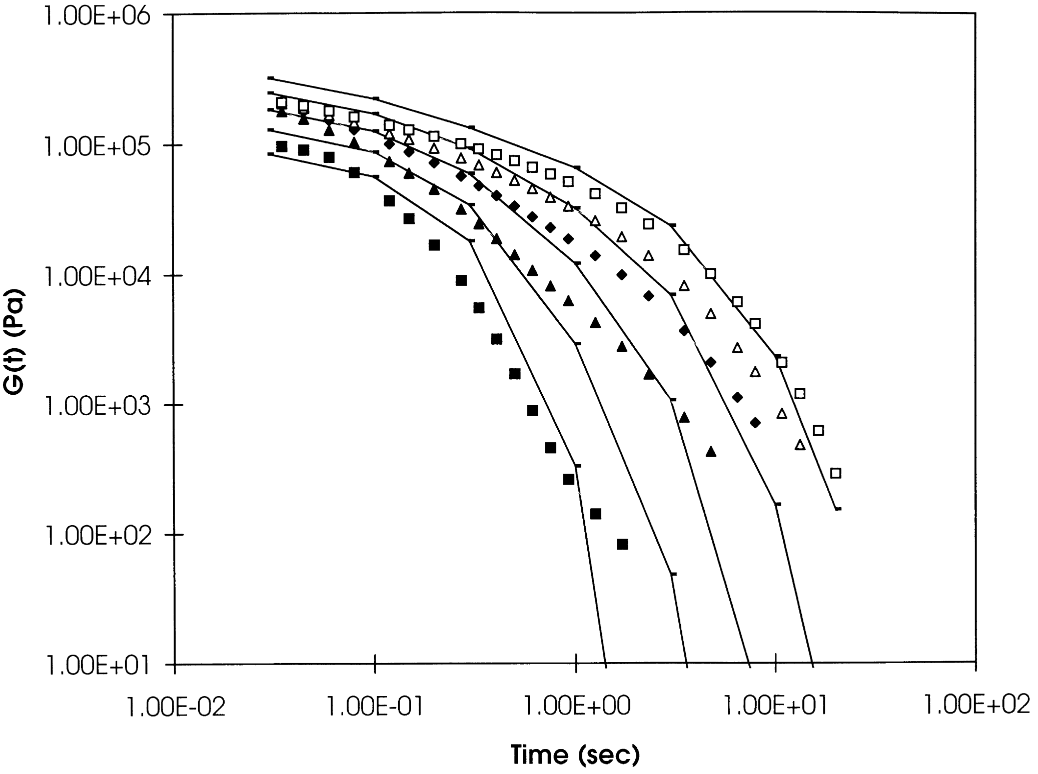

Figure 3 Relaxation modulus in shear, G(t), for blends of the three-Arm star with the linear polystyrene. Lines are McLeish and O'Connor theory. Points are the measured data for: 100% linear PS, ■; 75/25 linear/star, ▲; 50/50 linear/star, ◆; 25/75 linear/star, △; 100% star PS, □

slightly different G_0 values, as with linear and branched polyethylenes.

The theoretical fits of G(t) for these star–linear blends using the McLeish–O'Connor blending rule are shown with equations (2) and (3) using $b = 2$ in *Figure 3*, and with equations (2) and (4) in *Figure 4*. The fit of the Tsenoglou blending rule with the original power index of $a = 2$ is shown in *Figure 5*.

Discussion and conclusions

It is clear that the best overall theoretical fit to the

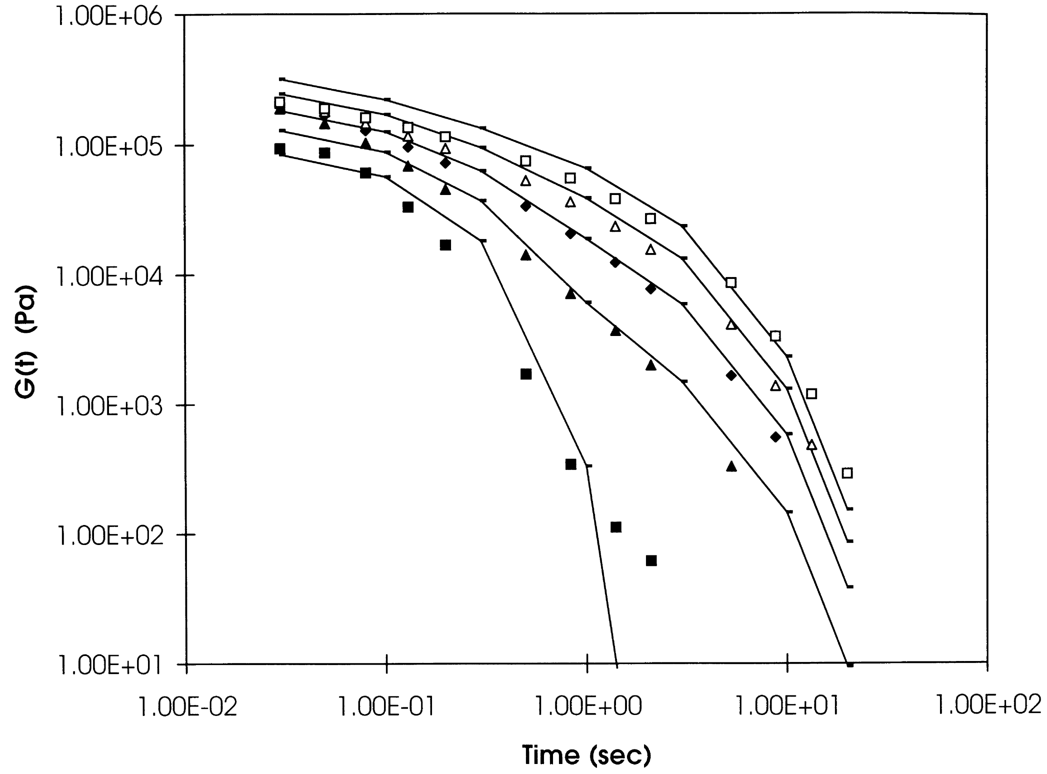

Figure 4 Relaxation modulus in shear, G(t), for blends of the three-arm star with the linear polystyrene. Lines are McLeish and O'Connor theory simplified for reduced cooperative relaxation. Points are the measured data with symbols as in *Figure 3*

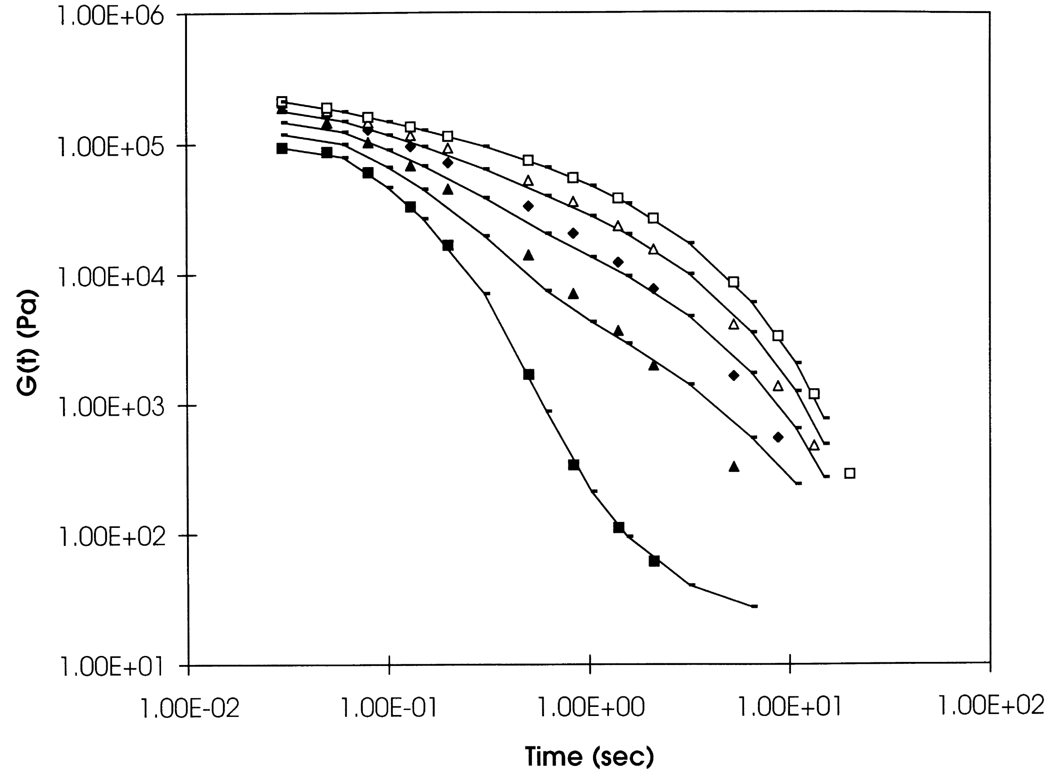

Figure 5 Relaxation modulus in shear, G(t), for blends of the three-arm star with the linear polystyrene. Lines are Tsenoglou theory. Points are the measured data with symbols as in *Figure 3*

experimental G(t) data is achieved with the simplified version of the McLeish and O'Connor blending rule (equations (2) and (4)), which is specific to these star–linear polymer blends. The relatively low molecular weight of the linear polystyrene allows it to relax largely by fluctuation in a primitive entangled path length, similarly to the star-arms before reptation intervenes, and therefore the contribution to cooperative relaxation within the blend is reduced or simplified. It is therefore appropriate that the simplified equation (4) in this blending rule should provide

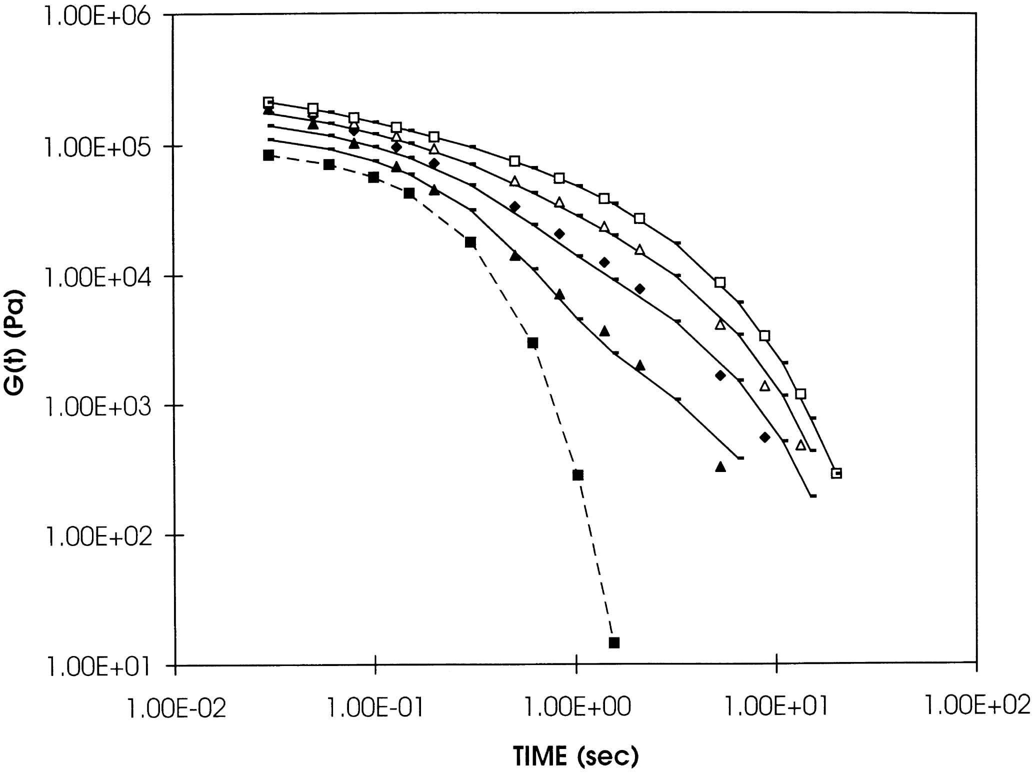

Figure 6 Relaxation modulus in shear, G(*t*), for blends of the three-arm star with the linear polystyrene. Lines are Tsenoglou theory using McLeish and O'Connor theory to calculate the linear polystyrene data (broken line). Points are the measured data with symbols as in *Figure 3*

the best fit. In addition the prediction is independent of the detail of experimental G(*t*) data for the 100% star and 100% linear polystyrene, which effectively form the boundary conditions with the Tsenoglou blending rule.

At longer times the relaxation of G(*t*) for the linear polystyrene reaches the minimum torsional limit of the Rheometrics RDA2 transducer, so the accuracy of data are restricted. The valid fit of the Tsenoglou theory at longer times may therefore be restricted. To explore this problem we have replaced the worst experimental data, for the linear polymer, by the linear polymer theoretical curve from the McLeish–O'Connor theory, and the resulting improvement in the fit of the Tsenoglou rule is shown in *Figure 6*. Within the limits of the data we observe that increasing the power index, from $a = 2$ to $a = 3$ for example, optimizes the fit of the Tsenoglou rule at longer times in preference to shorter times. We therefore speculate that while the original Tsenoglou rule with $a = 2$ is suited to linear polymer relaxation within a blend, a higher index, e.g. $a = 3$, may be more appropriate for the longer time scale of the retraction of star-arms or long chain branching, whenever an empirical approach is necessary, or a molecular theory unfeasible.

To achieve a more complete picture, and thereby a better understanding, of the way these two theories represent a blend of linear and star or linear and branched polymers, it will be essential to evaluate a range of star–linear polymer blends with widely differing molecular weight combinations. Recently, Milner and McLeish[10] calculated explicit relaxation spectra for monodisperse star polymer melt, including the weak X-dependence of the prefactors τ_0 in equations (3) and (4) and effects of unconstrained Rouse motion of the free end. Extension of these ideas to star–linear blends will sharpen our understanding of the role of constraint-release in these highly cooperative dynamics. It is anticipated that this may also explain why a modified Tsenoglou blending rule, with a dependent on the zero shear viscosities of the component polymers[7], proved useful with commercial linear and branched polyethylene blends.

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