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Simple constitutive models for linear and branched polymers

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Abstract

It is shown that several (single-mode) models (PTT, XPP) are basically special cases of the general network model. The XPP model [J. Rheol. 45 (2001) 823] is shown to give an identical response to a PTT model at high elongational rates, but the models differ in shear flow at high shear rates. The Giesekus term in the XPP model has practically no effect at any deformation rate except the generation of a second normal stress difference at small shear rates. The possibility of tailoring the shear flow response at high shear rates is explored. The results for the models are also given to show the effect of branching on the response in both transient and steady flows—elongation, shear, planar elongation and biaxial deformation. Finally, the fitting of data with multi-mode models is investigated.

Keywords: Constitutive models; Linear and branched polymers; XPP model; PTT model

1. Introduction

Considerable progress has been made in the last 40 years on constitutive modelling for viscoelastic flows [1], and much of this progress has been the direction of understanding the microstructural dynamics of long-chain molecules. For example, numerous reptation studies have shed light on how amorphous polymer melts behave [1]; older network theories based on “entanglements” [2], have made many contributions to the development of constitutive models for solutions and melts, and many successful models are based on network ideas. Both types of theory, network and reptation, use similar stress calculators for computing the stresses in the deforming materials [1–4] and hence, given the molecular configuration at a given instant and the forces in the molecules, both are able to predict macroscopic stress levels. Where the two types of theory differ is that traditional network theory introduces rates of network junction creation and destruction that are largely empirical, while the reptation theories are a branch of polymer physics, seeking a more fundamental approach from the molecular state. The initial Doi and Edwards [4] description was very simple, but in more recent developments much of this simplicity has been lost, some

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empiricism has reappeared and there are signs [5] that a rapprochement of the various points of view is occurring.

As to motivation for the paper, we note that the original PTT concept is now more than 25 years old and has not been significantly changed in this time, although it has been quite widely used. We believe it is time to reconsider it, in the context of new knowledge, especially with respect to branched molecules, that has been discovered in this interval. While polymer science continues to make progress towards the a priori prediction of rheological properties, we believe it is likely that simpler models, with some empirical latitude, will continue to be of practical use for a considerable time yet.

In this spirit, we re-examine the general network model [3,7] and several special cases of it in shearing and elongation. We shall discuss in detail the PTT [1] and Giesekus models [1,8] and the newer XPP model of Verbeeten et al. [6,9]. The latter is said to represent a reptation type model, the PTT model is based on network theory, and the Giesekus model actually stems from a dilute solution theory [1]. While it is recognized [1] that multiple relaxation mode models are essential for the realistic description of real polymers, we shall mainly consider single-mode models, so that the stress ($\boldsymbol{\sigma}$) will be given by

$$\boldsymbol{\sigma} = -p\boldsymbol{I} + 2\eta_s\boldsymbol{d} + \boldsymbol{\tau}, \tag{1}$$

where p is pressure, $\boldsymbol{I}$ the unit tensor, η_s a 'solvent' viscosity, $\boldsymbol{d}$ the rate of deformation tensor equal to $1/2(\boldsymbol{L} + \boldsymbol{L}^T)$, and $\boldsymbol{\tau}$ the extra-stress tensor to be found from the constitutive model. The velocity gradient tensor $\boldsymbol{L}$ is defined as $\boldsymbol{L} = (\nabla\boldsymbol{v})^T$(or $L_{ij} = \partial v_i/\partial x_j$), where $\boldsymbol{v}(\boldsymbol{x}, t)$ is the velocity field at place $\boldsymbol{x}$ at time t, and T denotes the transpose of a tensor; ∇ is the gradient operator. The flows are supposed to be isothermal and incompressible; inertia and gravity will be ignored, and the stress fields are homogeneous, so the mass and momentum equations are satisfied. The pressure p in Eq. (1) is therefore of no rheological significance and only normal stress differences and shear stresses will be reported. Hence we concentrate on the equations for $\boldsymbol{\tau}$, the constitutive equations.

Finally, the ability of the multi-mode PTT–XPP model to describe shear flow is investigated and the results are compared with the ones obtained by Verbeeten et al. [9].

2. The special models

According to Verbeeten et al. [6,9], the extended Pom-Pom model (XPP) can be written in the form, for a single mode,

$$\frac{\Delta\boldsymbol{\tau}}{\Delta t} + \boldsymbol{f}_{gs}(\boldsymbol{\tau}, \boldsymbol{d}) + \boldsymbol{\lambda}^{-1}(\boldsymbol{\tau})\boldsymbol{\tau} = 2G\boldsymbol{d}, \tag{2}$$

where $\Delta/\Delta t$ is the usual upper-convected time derivative, $\boldsymbol{\tau}$ the stress due to the mode, $\boldsymbol{d}$ the rate of deformation tensor, and G a shear modulus. The symbol $\boldsymbol{f}_{gs}$ is defined below and the tensor $\boldsymbol{\lambda}^{-1}$ is a function of stress invariants. The definition of the upper-convected derivative $\Delta\boldsymbol{\tau}/\Delta t$ is [1]

$$\frac{\Delta\boldsymbol{\tau}}{\Delta t} \equiv \frac{\partial\boldsymbol{\tau}}{\partial t} + (\boldsymbol{v}.\nabla)\boldsymbol{\tau} - \boldsymbol{\tau}\boldsymbol{L}^T - \boldsymbol{L}\boldsymbol{\tau}, \tag{3}$$

where $\boldsymbol{v}$ is the velocity field, and the velocity gradient $\boldsymbol{L}$ is defined above. If $\boldsymbol{f}_{gs} = 0$ and $\boldsymbol{\lambda} = \lambda\boldsymbol{I}$, then the Upper-Convected Maxwell [1] model is recovered. For the Giesekus model

$$\boldsymbol{f}_{gs} = \boldsymbol{0}, \qquad \boldsymbol{\lambda}^{-1} = \frac{1}{\lambda}\left[\frac{\alpha}{G}\boldsymbol{\tau} + \boldsymbol{I}\right], \tag{4}$$

where α is the usual Giesekus parameter [3].

There are many forms of the PTT model [1]; if a non-affine deformation is permitted,

$$\boldsymbol{f}_{\rm gs} = \xi(\boldsymbol{d\tau} + \boldsymbol{\tau d}). \tag{5}$$

The commonly used exponential-kernel form is

$$\boldsymbol{\lambda}^{-1} = \frac{1}{\lambda}\left[\exp\left(\frac{\varepsilon}{G}\mathrm{tr}\boldsymbol{\tau}\right)\right]\boldsymbol{I}, \tag{6}$$

where ξ and ϵ are dimensionless parameters. Often $\xi = 0$ in applications, so $\boldsymbol{f}_{\rm gs} = \boldsymbol{0}$ again.

One also has the linear PTT model, where $1 + \varepsilon \mathrm{tr}\,\boldsymbol{\tau}/G$ replaces the exponential form in Eq. (6); this is less useful for polymer melts [3].

For the single-equation formulation of the XPP model developed for branched molecules, Verbeeten et al. [6] give

$$\boldsymbol{f}_{\rm gs} = 0, \qquad \boldsymbol{\lambda}^{-1} = \frac{1}{\lambda_{\rm b}}\left[\frac{\alpha}{G}\boldsymbol{\tau} + F\boldsymbol{I} + G(F-1)\boldsymbol{\tau}^{-1}\right], \tag{7}$$

where

$$F(\boldsymbol{\tau}) = 2re^{\nu(\Lambda-1)}\left(1-\frac{1}{\Lambda}\right) + \frac{1}{\Lambda^2}\left[1-\frac{\alpha\mathrm{tr}(\boldsymbol{\tau}^2)}{3G^2}\right], \tag{8}$$

and

$$\Lambda = \sqrt{1+\frac{\mathrm{tr}\boldsymbol{\tau}}{3G}}; \qquad r = \frac{\lambda_{\rm b}}{\lambda_{\rm s}}, \qquad \nu = \frac{2}{q}, \qquad \lambda_{\rm b} = \lambda, \tag{9}$$

where q, an integer ≥ 1, is the number of arms of the branched molecule, and $\lambda_{\rm s}$ a time constant for stretch, $\lambda_{\rm b} = \lambda$ the usual linear relaxation time. Note that if $\mathrm{tr}\boldsymbol{\tau}/3G$ is less than -1, Λ becomes meaningless.

Note also that $F(\boldsymbol{\tau})$ is a function of $\mathrm{tr}\,\boldsymbol{\tau}$ and $\mathrm{tr}\,\boldsymbol{\tau}^2$, unlike the PTT model, where only $\mathrm{tr}\,\boldsymbol{\tau}$ is involved. The $\boldsymbol{f}_{\rm gs}$ is a PTT term, which we will usually set to zero for the following discussion, so that all the models have zero slip parameter (ξ) unless otherwise stated. Inserting (7) into (2) we find, for $\xi = 0$,

$$\frac{\Delta\boldsymbol{\tau}}{\Delta t} + \frac{1}{\lambda}\left[\frac{\alpha}{G}\boldsymbol{\tau}^2 + F\boldsymbol{\tau} + G(F-1)\boldsymbol{I}\right] = 2G\boldsymbol{d}. \tag{10}$$

The second term in Eq. (10) is a Giesekus form. The third is a PTT form and the extra factor $G(F-1)\boldsymbol{I}$ represents the difference between XPP and PTT models, when $\alpha = 0$.

It is convenient to make all models dimensionless using the time constant λ and the modulus G, so that $(t/\lambda) \sim t$, $(\boldsymbol{\tau}/G) \sim \boldsymbol{\tau}$, $(\lambda\boldsymbol{d}) \sim \boldsymbol{d}$. Then we find:

(a) *Exponential PTT model*

$$\frac{\Delta\boldsymbol{\tau}}{\Delta t} + \xi(\boldsymbol{d\tau} + \boldsymbol{\tau d}) + \boldsymbol{\tau}\exp(\varepsilon\mathrm{tr}\boldsymbol{\tau}) = 2\boldsymbol{d}, \tag{11}$$

which contains only two parameters (or one free one, if $\xi = 0$).

(b) *Giesekus model*

In this case we get

$$\frac{\Delta\boldsymbol{\tau}}{\Delta t} + (\alpha\boldsymbol{\tau} + \boldsymbol{I})\boldsymbol{\tau} = 2\boldsymbol{d}, \tag{12}$$

which contains only one parameter.

(c) *XPP model*

Here we find

$$\frac{\Delta \boldsymbol{\tau}}{\Delta t} + \xi(\boldsymbol{d\tau} + \boldsymbol{\tau d}) + \left[\alpha \boldsymbol{\tau}^2 + F\boldsymbol{\tau} + (F-1)\boldsymbol{I}\right] = 2\boldsymbol{d}, \tag{13}$$

which appears to contain only two parameters (one if $\xi = 0$), but from (8) and (9) we see that F contains two extra parameters. So r and ν are extra parameters designed to include branching [6]. The Giesekus parameter α generates the second normal stress difference in shearing and we expect that it is O(0.1). For very large stresses, with $\xi = 0$, we find, in shear-free flows, that Eq. (13) reduces to

$$\frac{\Delta \boldsymbol{\tau}}{\Delta t} + F\boldsymbol{\tau} \approx 2\boldsymbol{d}, \tag{14}$$

where $F = 2re^{\nu(\Lambda-1)}(1 - 1/\Lambda)$. Eq. (14) is a PTT form with tr $\boldsymbol{\tau}$ as argument of an exponential form F. In the limit of a fast elongational flow (large $\dot{\varepsilon}$), where we know $\tau_{xx} \approx \mathrm{tr}\,\boldsymbol{\tau}$, $\tau_{yy} = \tau_{zz} \to 0$, then in this form

$$-2\dot{\varepsilon}\tau_{xx} + 2r\exp\left(\nu\sqrt{\frac{\tau_{xx}}{3}}\right)\tau_{xx} \approx 0, \tag{15}$$

resulting in $\tau_{xx} \approx (3/\nu^2)[\ln(\dot{\varepsilon}/r)]^2$ and hence

$$\eta_{\mathrm{T}} \approx \frac{\tau_{xx}}{\dot{\varepsilon}} \approx \frac{3}{\nu^2\dot{\varepsilon}}\left[\ln\left(\frac{\dot{\varepsilon}}{r}\right)\right]^2. \tag{16}$$

With the usual exponential PTT kernel we get $\eta_{\mathrm{T}} \approx (\ln\dot{\varepsilon})/\dot{\varepsilon}$, so there is a little difference between the XPP and the exponential PTT models at extremely high elongation rates. We shall develop slightly better estimates of η_{T} in Section 4 for the XPP model. To set these models in context, we now review the general network model.

3. General network model

We recall that the differential form of the so-called general network model [3,7] is, in dimensionless form for the isothermal case

$$\frac{\Delta \boldsymbol{\tau}}{\Delta t} + \xi(\boldsymbol{d\tau} + \boldsymbol{\tau d}) + H(\langle h^2\rangle)\boldsymbol{\tau} = G_1\boldsymbol{I}, \tag{17}$$

where H and G_1, are given functions of $\langle h^2\rangle$, the average of the mean square of the network linkage vectors (h). In this equation H is a (dimensionless) function governing to the rate of destruction of junctions—the larger H is, so the destruction is more rapid—and G_1, also dimensionless, is related to the rate of creation of junctions. To obtain a closed form constitutive equation it is supposed that tr $\boldsymbol{\tau} \propto \langle h^2\rangle$, so that $\langle h^2\rangle$ can be eliminated in terms of the stresses. We now assume $\boldsymbol{S} = \boldsymbol{\tau} - a\boldsymbol{I}$, where a is a constant; recall only normal stress differences for $\boldsymbol{S}$ and $\boldsymbol{\tau}$ are rheologically significant so $\boldsymbol{S}$ and $\boldsymbol{\tau}$ are essentially the same functions. Now eliminate $\boldsymbol{\tau}$ from (17) and we find

$$\frac{\Delta \boldsymbol{S}}{\Delta t} + \xi(dS + Sd) + H\boldsymbol{S} + (aH - G_1)\boldsymbol{I} = 2a\boldsymbol{d}(1-\xi), \tag{18}$$

If we set $H = F$ (F as in (15)); $a = (1-\xi)^{-1}$, and $G_1 = 1 + \xi F/(1-\xi)$, we get

$$\frac{\Delta \boldsymbol{S}}{\Delta t} + \xi(dS + Sd) + F\boldsymbol{S} + (F-1)\boldsymbol{I} = 2\boldsymbol{d}, \tag{19}$$

which agrees with (13). Thus the XPP model is a special case of the general network model, plus a Giesekus term. Clearly, the PTT model is also a special case of the general network model; here $G_1 = F/(1-\xi)$. We can consider the network model for arbitrary H and G_1.

In a steady elongational motion where $\boldsymbol{\tau} = \mathrm{diag}[\sigma_1, \sigma_2, \sigma_2]$, $\boldsymbol{L} = \mathrm{diag}[\dot{\varepsilon}, -\dot{\varepsilon}/2, -\dot{\varepsilon}/2]$, (17) becomes (with $\xi = 0$)

$$-2\dot{\varepsilon}\sigma_1 + \sigma_1 H = G_1, \qquad \dot{\varepsilon}\sigma_2 + \sigma_2 H = G_1, \qquad \sigma_3 = \sigma_2, \tag{20}$$

and tr $\boldsymbol{\tau} \equiv \sigma_1 + 2\sigma_2$, so that $\sigma_2 = G_1/(H + \dot{\varepsilon})$, $\sigma_1 = G_1/(H - 2\dot{\varepsilon})$. In order that σ_1 remains positive, $H > 2\dot{\varepsilon}$, so H must increase as tr $\boldsymbol{\tau}$ and $\dot{\varepsilon}$ increase. Considering Eq. (20), supposing that $\sigma_1 \gg \sigma_2$,

$$H(\sigma_1) \approx 2\dot{\varepsilon} \tag{21}$$

Hence only H governs the high elongational rate behaviour of the material—G_1 is not involved. If the form of H is given, one can then find σ_1 from (21). For example, if $H = \exp(\varepsilon \mathrm{tr}\, \boldsymbol{\tau})$, (the exponential PTT model) then, $\exp(\varepsilon\sigma_1) \approx 2\dot{\varepsilon}$, or $\sigma_1 \approx (\ln 2\dot{\varepsilon})/\varepsilon$, and σ_2 is of $\mathrm{O}(1/\dot{\varepsilon})$, which is small [1].

Similarly in steady shearing where,

$$\boldsymbol{\tau} = \begin{pmatrix} \sigma_1 & \tau & 0 \\ \tau & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{pmatrix}; \qquad \boldsymbol{L} = \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

we find

$$-2\dot{\gamma}\tau + H\sigma_1 = G_1, \qquad -\dot{\gamma}\sigma_2 + H\tau = 0, \qquad H\sigma_2 = G_1, \qquad H\sigma_3 = G_1. \tag{22}$$

Hence, $\sigma_2 - \sigma_3 = N_2 = 0$, and tr $\boldsymbol{\tau} = \sigma_1 + 2\sigma_2$. Eliminating σ_2 and $\boldsymbol{\tau}$ (assuming G_1 is not larger than H) then in the high-shearing limit, we have: $\sigma_1 \approx 2\dot{\gamma}^2 G_1/H^3$.

Thus if G_1 and H are known forms, σ_1 can be found. For example, if $G_1 = H$ (PTT models) and $H = \exp(\varepsilon \mathrm{tr}\, \boldsymbol{\tau})$ (the exponential PTT model) then

$$\sigma_1 = 2\dot{\gamma}^2 \exp(-2\varepsilon\sigma_1), \quad \sigma_1 \sim \frac{\ln\dot{\gamma}}{\varepsilon} \tag{23}$$

which leads to the known result

$$\frac{\tau}{\dot{\gamma}} \sim \frac{\eta}{\eta_0} \sim \dot{\gamma}^{-1}\left[\frac{\ln\dot{\gamma}}{\varepsilon}\right]^{1/2} \tag{24}$$

4. Response functions

We consider further the kinds of response that can be obtained from the models at high rates of deformation. For very high elongation rates $\lambda\dot{\varepsilon} \equiv W_i \to \infty$, or in dimensionless form simply $\dot{\varepsilon} \to \infty$, the results for the exponential and linear PTT models and the Giesekus model are known [1,8] and are given in Table 1. For the XPP model ($\xi = 0$) we can proceed as follows. For steady, homogeneous

Table 1
Behaviour at high deformation rates

Model	Elongation (η_{T}/η_0)	Shear (η/η_0)
Exponential PTT	$\varepsilon^{-1}(\ln W_i)/W_i$	$[(\ln W_i)/2\varepsilon]^{1/2}/W_i$
Linear PTT [1]	$2/\varepsilon$	$(2\varepsilon)^{-1/3}(W_i)^{-2/3}$
Giesekus [8]	$2/\alpha$	$[(1-\alpha)/\alpha]^{1/2}/W_i$
XPP	$\dfrac{3}{W_i}\left[\left\{1+\nu^{-1}\ln\dfrac{W_i}{r}\left(1+\dfrac{\nu}{\ln(W_i/r)}\right)\right\}^2-1\right]$	$(6\nu^2)^{-2/3}W_i^{-4/3}\left[\ln\left(\dfrac{W_i^2}{4r^3}\right)\right]^{4/3}$
PTT–XPP	Same as XPP	$W_i^{-1}\sqrt{\dfrac{3}{2}}\left[\left(1+\nu^{-1}\left(\ln\dfrac{W_i}{r\sqrt{2}}-\ln\ln\dfrac{W_i}{r\sqrt{2}}\right)\right)^2-1\right]^{1/2}$

The table shows the value of $(\sigma_{11}-\sigma_{22})/\eta_0\dot{\varepsilon}(\equiv\eta_T/\eta_0)$; (1 is the elongation direction, 2 is the radial direction) as a function of $W_i=\lambda\dot{\varepsilon}$; $\dot{\varepsilon}$ is the elongation rate and σ_{ij} the stresses, η_0 the zero-shear rate viscosity and λ the relaxation time. Also shown are the viscosity ratios for simple shearing, $W_i=\lambda\dot{\gamma}$. (In the text $W_i=\lambda\dot{\varepsilon}$(or $\lambda\dot{\gamma}$) is written in dimensionless form as $\dot{\varepsilon}$(or $\dot{\gamma}$)). The dimensionless constants ε (exponential and linear PTT models), α (Giesekus and XPP models), ν and r (XPP and PTT–XPP models) are defined in the text.

elongation (13) becomes (dimensionless form)

$$\alpha\sigma_1^2+(F-2\dot{\varepsilon})\sigma_1+F-1=2\dot{\varepsilon}\quad(\text{axial}),\tag{25}$$

and

$$\alpha\sigma_2^2+(F+\dot{\varepsilon})\sigma_2+F-1=-\dot{\varepsilon}\quad(\text{radial}),\tag{26}$$

where $\boldsymbol{\tau}=\mathrm{diag}[\sigma_1,\sigma_2,\sigma_2]$ in this case. As $\dot{\varepsilon}$ becomes very large we suppose σ_2 is of O(1); since σ_1 is supposed to become very large, then F also becomes large. We can take $\sigma_2=-1$ in (26) thereby satisfying the balance of the F and $\dot{\varepsilon}$ terms, with a residual of $\mathrm{O}(\alpha-1)$, which will be ignored. Hence, as the axial stress becomes large, $\mathrm{tr}\,\boldsymbol{\tau}\to\sigma_1$. In (25) we note that F is of order $\exp(\nu\sqrt{\sigma_1})$ as $\sigma_1\to\infty$, and so all terms except $2\sigma_1\dot{\varepsilon}$ are less than $\sigma_1 F$, and will be ignored. Hence$F\approx 2\dot{\varepsilon}$, which is a single equation for σ_1. Now as $\sigma_1\to\infty$, and hence $\Lambda\to\infty$,

$$\left(1-\frac{1}{\Lambda}\right)\exp[\nu(\Lambda-1)]\approx\frac{\dot{\varepsilon}}{r},\tag{27}$$

where $\Lambda\approx((1+\sigma_1)/3)^{1/2}$. To a first approximation, ignoring $1/\Lambda$, we find $\Lambda\approx 1+\nu^{-1}\ln(\dot{\varepsilon}/r)$,or

$$\sigma_1\approx 3\left[1+\nu^{-1}\ln\frac{\dot{\varepsilon}}{r}\right]^2-3.\tag{28}$$

When $r=3$, $\upsilon=1$, $\dot{\varepsilon}=10^3$, this gives a value of $\sigma_1=136$. The computed value is 144. A slight improvement can be obtained by retaining the $1-1/\Lambda$ term in (27) and using (28) to find

$$\sigma_1\approx 3\left[1+\nu^{-1}\ln\left\{\frac{\dot{\varepsilon}}{r}\left(1+\frac{\nu}{\ln(\dot{\varepsilon}/r)}\right)\right\}\right]^2-3.\tag{29}$$

This gives $\sigma_1=143$ in dimensionless units.

The point to be observed is that at very high elongation rates the terms containing α play no part in the solution, nor do the $F-1$ terms. If we consider the PTT family of equations, $\Delta\boldsymbol{\tau}/\Delta t + \boldsymbol{\tau}\, f(\mathrm{tr}\boldsymbol{\tau}) = 2\boldsymbol{d}$, then the solution of the XPP equations at high elongation rates is identical to that of a PTT model where

$$f = \frac{1}{\Lambda^2} + 2r\left(\frac{\Lambda-1}{\Lambda}\right)\exp\left[\nu(\Lambda-1)\right], \tag{30}$$

and $\Lambda = (1+(1/3)\mathrm{tr}\boldsymbol{\tau})^{1/2}$. Therefore, if we neglect the Giesekus ($\alpha = 0$) and the $(F-1)\boldsymbol{I}$ terms in the XPP model, we generate a new type of PTT model (PTT–XPP). This is shown in Fig. 1, where PTT–XPP is a curve giving results for such a model with $\nu = 1$, $r = 3$. The full XPP curve uses all terms in the equation, with $\alpha = 0.15$, $\nu = 1$, $r = 3$. Also included in Fig. 1 is the PTT ($\varepsilon = 0.25$) result, and the XPP curve where $\alpha = 0$.

One sees that

(1) The Giesekus term in the XPP model makes little difference at any elongation rate.
(2) The PTT–XPP is extremely close to the XPP curves.
(3) The exponential PTT model (and the Giesekus model) have different asymptotic behaviours to the XPP models.

With regard to the Giesekus and $\alpha(\mathrm{tr}\,\boldsymbol{\tau}^2)$ terms in the XPP model, note that at high deformation rates $\mathrm{tr}\boldsymbol{\tau}^2 \approx (\mathrm{tr}\boldsymbol{\tau})^2$, so the F-dependence is similar to the PTT kernel dependence.

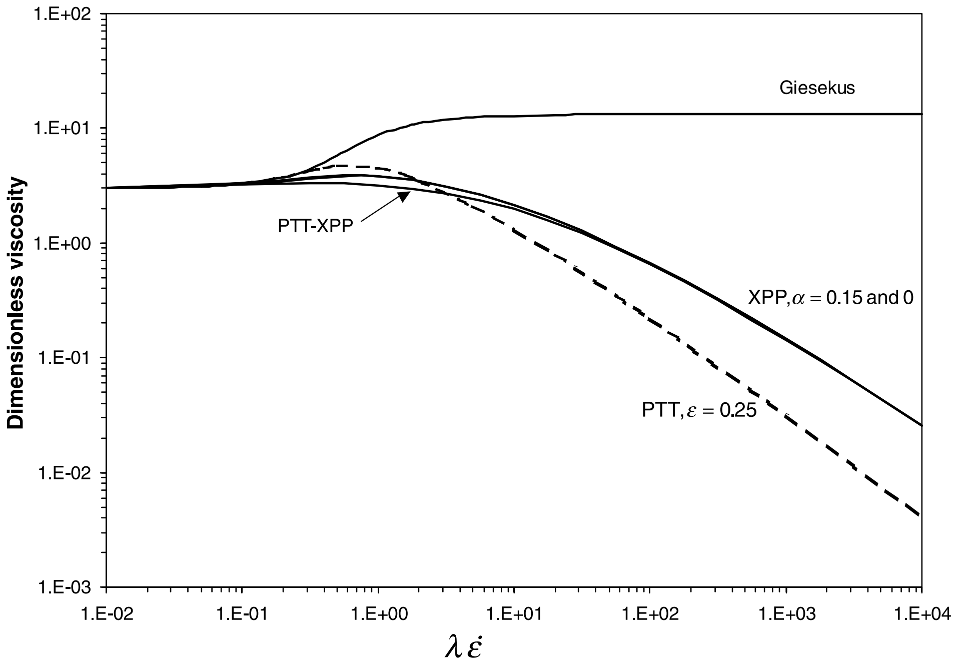

Fig. 1. Steady state values for dimensionless elongational viscosity vs. Weissenberg number for Giesekus, PTT (exponential, $\varepsilon = 0.25$), XPP and PTT–XPP models ($\nu = 1$, $r = 3$). α has an insignificant effect on the viscosity values. The PTT–XPP is extremely close to the XPP curves.

For large shear rates, we may proceed in a similar manner. In simple shearing

$$\tau = \begin{pmatrix} \sigma_1 & \tau & 0 \\ \tau & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

we will have the following two equations [1] for all PTT models (when $N_2 = 0$ and $\xi = 0$)

$$-2\tau\dot{\gamma} + \sigma_1 f = 0, \quad \tau f = \dot{\gamma},$$

Eliminating f and then τ, knowing that $\mathrm{tr}\boldsymbol{\tau} \approx \sigma_1$:

$$\sqrt{\sigma_1} f = \sqrt{2}\dot{\gamma}.$$

For the case when f is given by $\exp(\varepsilon\sigma_1)$, we find, for large $\dot{\gamma}$

$$\sigma_1 = \varepsilon^{-1}\ln(\dot{\gamma}), \qquad \tau = \left\{0.5\varepsilon^{-1}\ln(\dot{\gamma})\right\}^{1/2}, \tag{31}$$

computation gives, at $\dot{\gamma} = 10^4$, $\tau = 3.96$; Eq. (31) gives 4.29.

The asymptotic results for the PTT and Giesekus models are given in Table 1, column 3. Here N_2 is negative if $\xi > 0$ for the PTT family, and also for the Giesekus model. For the XPP model ($\xi = 0$), the equations reduce to

$$\alpha(\sigma_1^2 + \tau^2) - 2\dot{\gamma}\tau + F\sigma_1 + F - 1 = 0, \tag{32}$$

$$-\dot{\gamma}\sigma_2 + \alpha(\sigma_1 + \sigma_2)\tau + \tau F = \dot{\gamma}, \tag{33}$$

$$\alpha(\tau^2 + \sigma_2^2) + \sigma_2 F + F - 1 = 0, \tag{34}$$

$$\alpha(\sigma_3^2) + F\sigma_3 + F - 1 = 0. \tag{35}$$

For large shear rates, F is exponentially large so (34) and (35) tell us that, ignoring the α-terms, $\sigma_3 = \sigma_2 \approx -1 + 1/F$, and (33) becomes $\tau = \dot{\gamma}/F^2$. Substituting this in (32), with $\alpha = 0$, gives (neglecting F with respect to $\sigma_1 F$) the result

$$\sigma_1 \approx 2\dot{\gamma}^2/F^3. \tag{36}$$

For large shear rates, $F = 2re^{\nu(\Lambda-1)}(1 - \Lambda^{-1})$, and so we conclude

$$N_1 \approx \sigma_1 \approx \frac{1}{3}\left[\nu^{-1}\ln\left(\frac{\dot{\gamma}^2}{4r^3}\right)\right]^2, \tag{37}$$

and

$$\eta \approx \frac{\tau}{\dot{\gamma}} \approx (6\nu^2)^{-2/3}\dot{\gamma}^{-4/3}\left[\ln\left(\frac{\dot{\gamma}^2}{4r^3}\right)\right]^{4/3}. \tag{38}$$

Thus the viscosity curve decreases faster than $\dot{\gamma}^{-1}$, and the single-mode XPP model shows a static instability in shear as does the original Doi and Edwards model [1]. The estimate (38) shows reasonable agreement with computation: for $\dot{\gamma} = 10^4$, $\upsilon = 1$ (two branches), $r = 3$, we find $\eta = 0.46 \times 10^{-5}$, whereas computation gives ($\alpha = 0$) 0.45×10^{-5}; if $\alpha = 0.15$ computation gives 0.48×10^{-5}, so the effect of α is small at high rates, and can be neglected there.

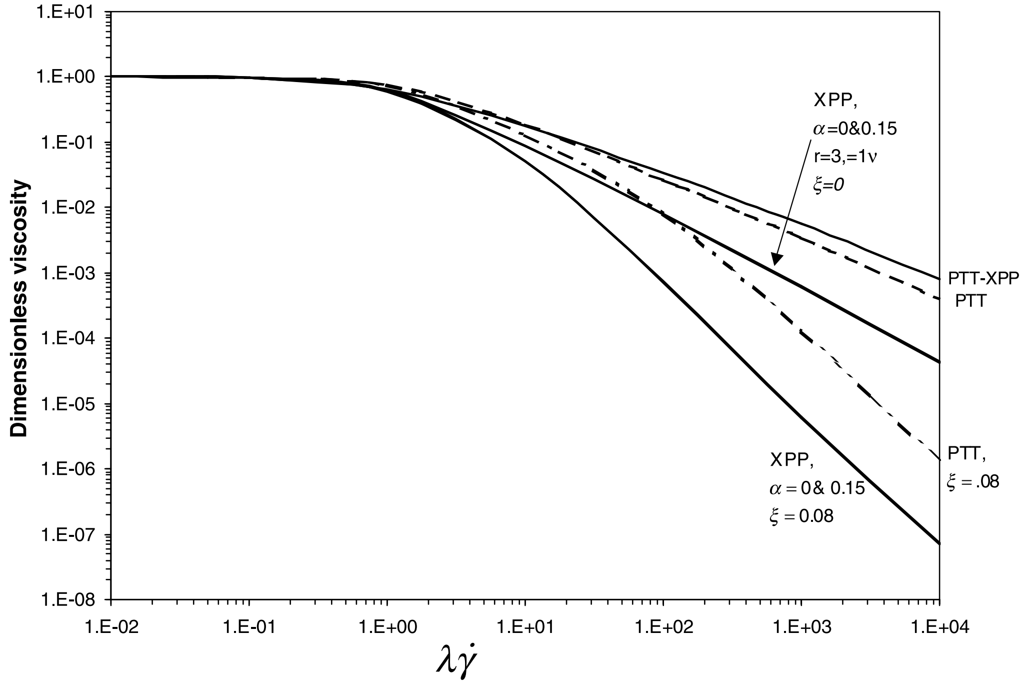

Fig. 2. Steady state values for dimensionless shear viscosity vs. Weissenberg number for Giesekus, PTT (exponential, $\varepsilon = 0.25$), XPP and PTT–XPP models ($\nu = 1$, $r = 3$). XPP shows a more rapid shear thinning behaviour. α has an insignificant effect on the viscosity values, whereas ξ has an important effect on the shear results.

We have seen that the response at high elongation rates is identical to the XPP (Fig. 1), whether α is zero or not, while the shear behaviour differs considerably (Table 1), since the viscosity of the PTT–XPP model behaves like ${W_i}^{-1}\ln(W_i)$ at high shear rates, whereas that of the XPP behaves like ${W_i}^{-4/3}(\ln W_i)^{4/3}$. Of course, if $\xi \neq 0$, much more rapid shear thinning of the PTT model ($\eta/\eta_0 \approx \dot{\gamma}^{-2}$) results (see Fig. 2; here $\varepsilon = 0.25$, $\xi = 0.08$).

At low shear rates all models behave like a Newtonian fluid (Fig. 2). Those models with $\alpha \neq 0$ (Giesekus, XPP) show a non-zero second normal stress difference ($N_2 = \tau_{yy} - \tau_{zz}$). The Giesekus result gives the ratio $N_2/N_1 = -\alpha$ as $\lambda\dot{\gamma} \to 0$ and $N_2/N_1 \to 0$ as $\lambda\dot{\gamma} \to \infty$. Here $N_1 = \tau_{xx} - \tau_{yy}$ as usual. All of the PTT models (exponential PTT, linear PTT, PTT–XPP) and the XPP model with $\alpha = 0$ show $N_2 = 0$.

The main points to note from Fig. 2 are

(1) The XPP models with $\alpha = 0.15$ and $\alpha = 0$ scarcely differ, except for the small N_2.
(2) There is considerable difference between the PTT–XPP and the XPP models.
(3) The XPP models shear-thin very rapidly $\sim \dot{\gamma}^{-4/3}$ at large Weissenberg numbers, so a single-mode XPP model is statically unstable [1,10].
(4) The slip coefficient ξ has an important effect on the shear results (see also Fig. 10).

The disagreement between the XPP and PTT–XPP models at high shear rates is unexpected, because the results agree in elongational flow. By looking at the general network model (Eq. (17)) we see that, broadly speaking, the network destruction function $H(\equiv F$ when $\xi = 0)$ controls the elongation response

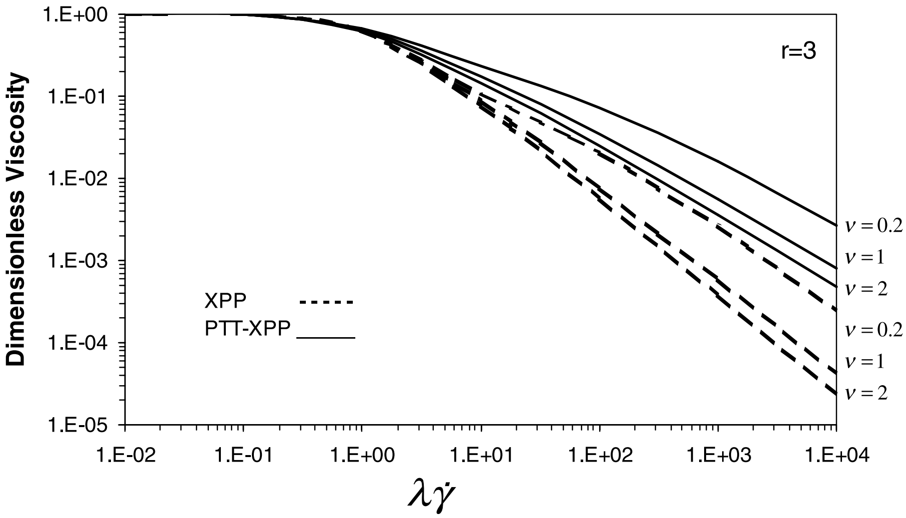

Fig. 3. Effect of $\nu = 2/q$ on the responses of XPP and PTT–XPP models in shear flow. $\xi = 0$ and $r = 3$ for all curves. For both models, an increase in number of arms of the branched molecule results in a slower shear thinning behaviour.

at high elongation rates. The G_1 function (network creation term) is 1 for the XPP model, and $G_1 = F$ for the PTT model, so the large shear rate behaviour is governed by G_1 and H together, and so a difference is predicted with the PTT giving a larger viscosity at a given shear rate with a given H.

We can illustrate this by assuming the XPP form of F (Eq. (8)). This sets the elongational response at high rates. The shear stress τ and the first normal stress σ_1 are respectively given by $\tau = \dot{\gamma} G_1/F^2$, $\sigma_1 = 2\dot{\gamma}^2 G_1/F^3$.

These can be combined to give

$$G_1 = \frac{2\tau^2 H}{\sigma_1}. \tag{39}$$

If $G_1 = 1$, then the asymptotic XPP formula $\tau \propto \dot{\gamma}^{-1/3}$ results; if $G_1 = F$ (PTT case) then $\tau \propto \ln \dot{\gamma}$. We can choose to maintain $\eta/\eta_0 \propto \dot{\gamma}^{-1}$ or $\tau(=\tau_{\max})$ as the shear rate becomes large, and in this case we have a result which lies between the XPP and PTT–XPP models. To achieve this, we see from (39) that asymptotically we need

$$G_1 = \frac{2\tau_{\max}^2 F}{\mathrm{tr}\boldsymbol{\tau}}. \tag{40}$$

Many more intermediate cases can be constructed; and in fact, the H function could also be chosen empirically to match the elongational behaviour if suitable data were available.

Figs. 3–6 show the response of the PTT–XPP and XPP models for various parameters, indicating the effect of r and ν on the response in elongation and shear. The planar elongation of the two models is essentially the same and so is the biaxial result (Fig. 7). Here we regard the biaxial flow as a negative elongation rate ($\dot{\varepsilon} < 0$), so the viscosity quoted relates to $(\sigma_1 - \sigma_2)/\dot{\varepsilon}$ in dimensionless terms, where σ_2 is now the large (radial) term of the stress, and σ_1 is small and compressive.

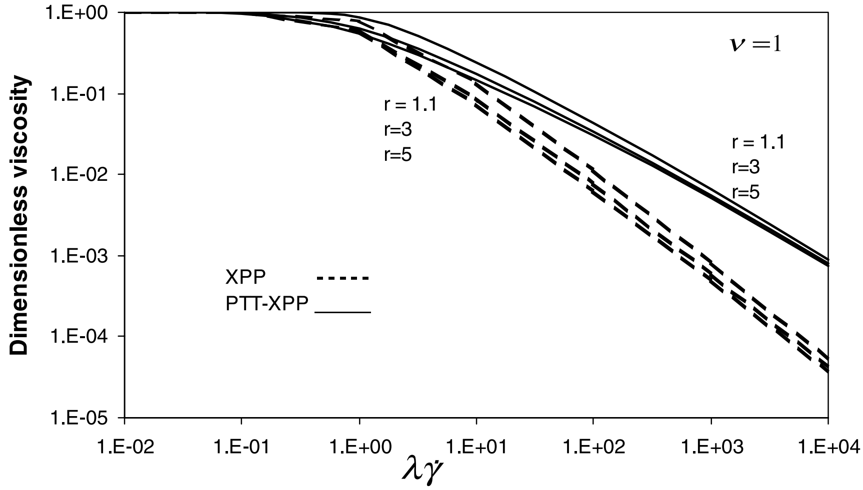

Fig. 4. Effect of $r = \lambda/\lambda_s$ on the responses of XPP and PTT–XPP models in shear flow. When the time constant for stretch (λ_s) is changed, both models give almost the same results for viscosity at high shear rates. $\xi = 0$ and $\nu = 1$ for all curves (two arms for each molecule).

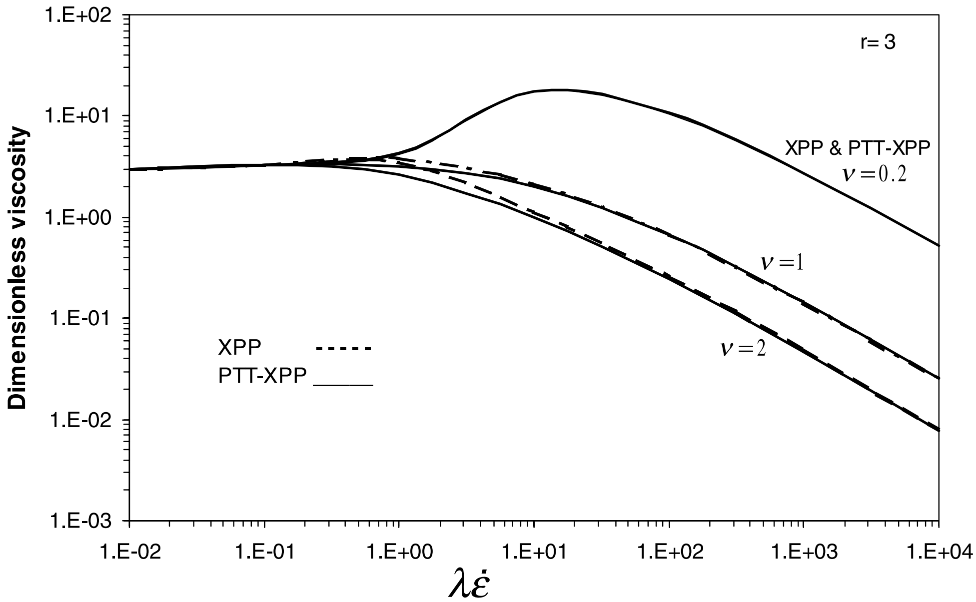

Fig. 5. Effect of $\nu = 2/q$ on the responses of XPP and PTT–XPP models in elongational flow. While the number of arms has a significant effect on elongational viscosity, there is little difference between the responses of the two models for each value of ν. Here $\xi = 0$ and $r = 3$ for all curves.

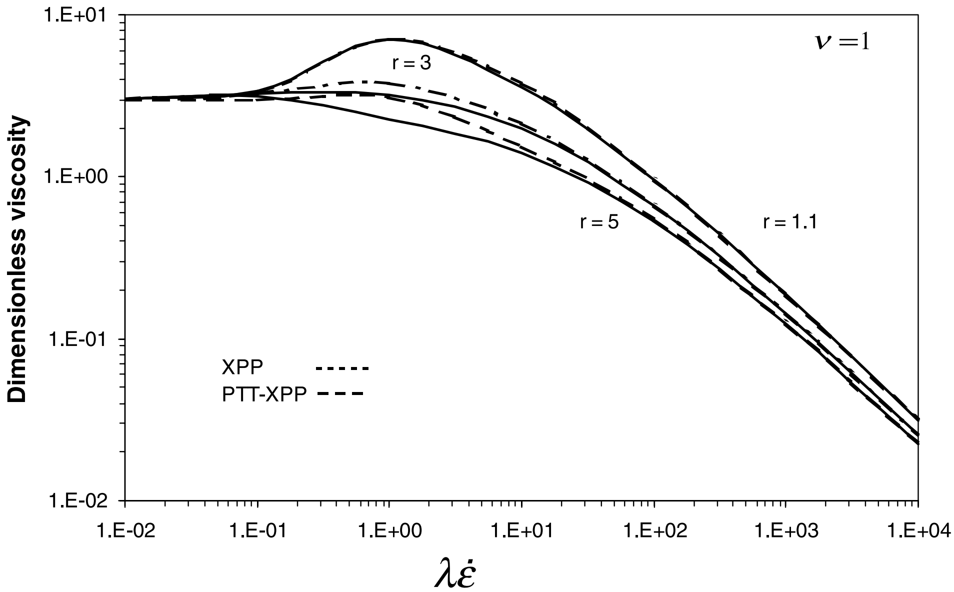

Fig. 6. Effect of $r = \lambda/\lambda_s$ on the responses of XPP and PTT–XPP models in elongational flow. r has an insignificant effect on the viscosity at high elongational rates. $\xi = 0$ and $\nu = 1$ for all curves (two arms for each molecule).

All of the above curves were integrated using a standard Runge–Kutta routine which produced the six stress components as a function of time for a given fixed kinematics.

From the results in Fig. 6, we note the similarity between the PTT and XPP results at medium ($\dot{\varepsilon} \sim 1$) elongational rates, where peaks may be found depending on the values of the parameters. Hence practical curve-fitting of elongational data with a given set of relaxation times can be done with either the XPP or PTT models. Substantial differences can only lie in shearing. The responses in transient flows are given in Figs. 8–11; here $\nu = 1$ and $r = 3$ in all cases. The dimensionless σ_{22} stress is small (<1 in magnitude) in all cases.

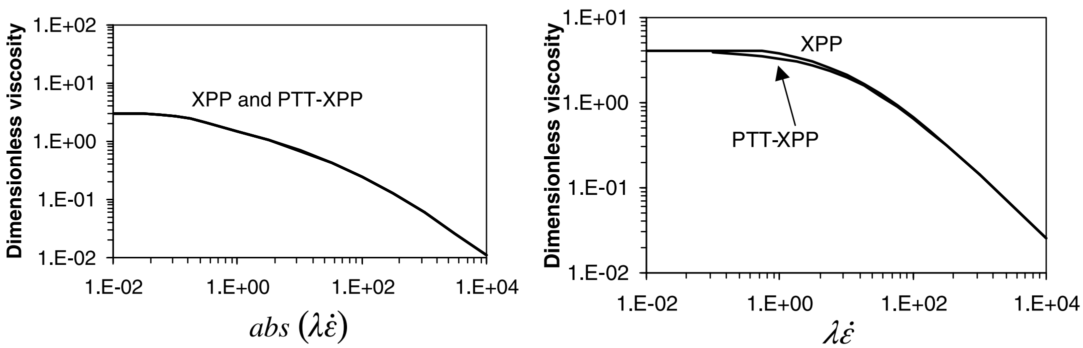

Fig. 7. Steady state values for dimensionless viscosity for XPP and PTT–XPP models in biaxial flow (left) and in planar flow (right). The PTT–XPP curves are very close to the XPP curves ($\nu = 1$, $r = 3$). α has an insignificant effect on the viscosity values of the XPP model.

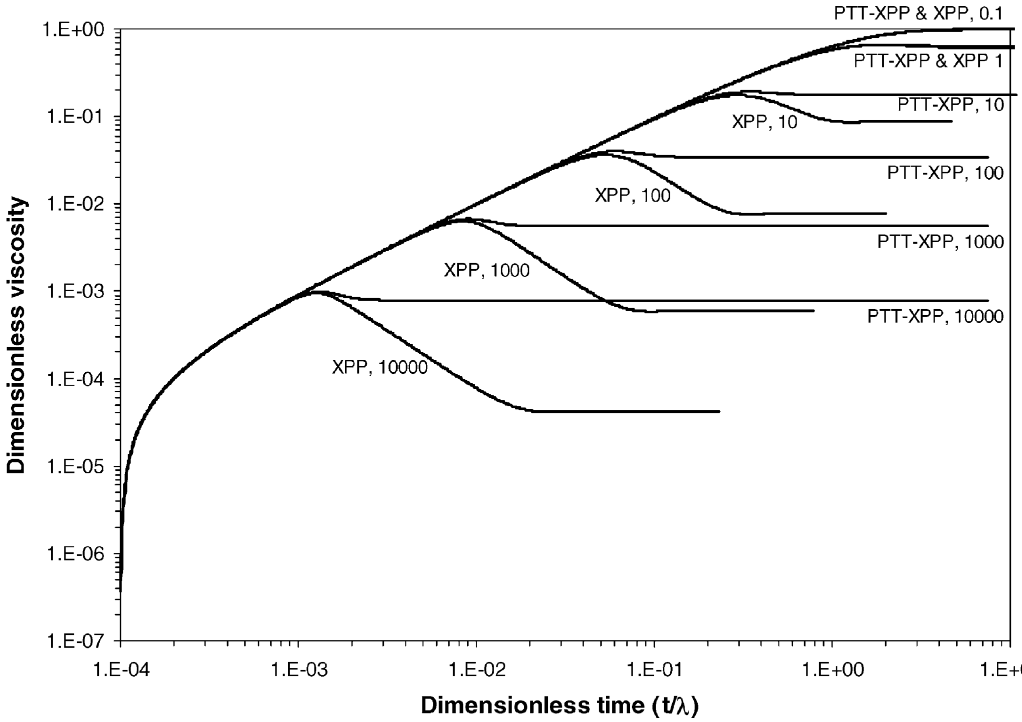

Fig. 8. The responses of XPP and PTT–XPP models in transient shear flow ($\nu = 1$, $r = 3$ and $\xi = 0$). Numbers attached to each model refer to the dimensionless shear rate value; both viscosity and time are dimensionless. Transient responses show overshoots in shear.

The performance of the multi-mode PTT–XPP model in shear flow has also been investigated using the linear and non-linear parameters used by Verbeeten et al. [9] (shown in Table 2). The results of the XPP and PTT–XPP models are very close (Figs. 12 and 13) even for high shear rates. The discrepancies between experiment and the PTT–XPP model could be further reduced if the parameters of the model in Table 2 were optimised for the PTT–XPP model. Furthermore, only four modes are used; this number can be increased.

Table 2
Linear and non-linear parameters used by Verbeeten et al. [9], for fitting of the DSM Stamylan LD 2008 XC43 LPDE melt

Mode i	Maxwell parameter		XPP		
	G_i (Pa)	λ_i (s)	$q_i = 2/\nu_i$	$\lambda_{b,j}/\lambda_{s,I}$	$\alpha_i = 0.15\nu_i$
1	7.2006E+4	3.8946E−3	1	7.0	0.3
2	1.5770E+4	5.1399E−2	1	5.0	0.3
3	3.3340E+3	5.0349E−1	2	3.0	0.15
4	3.008E+2	4.5911	10	1.1	0.03

The parameters have been used for both the multi-mode XPP and PTT–XPP models.

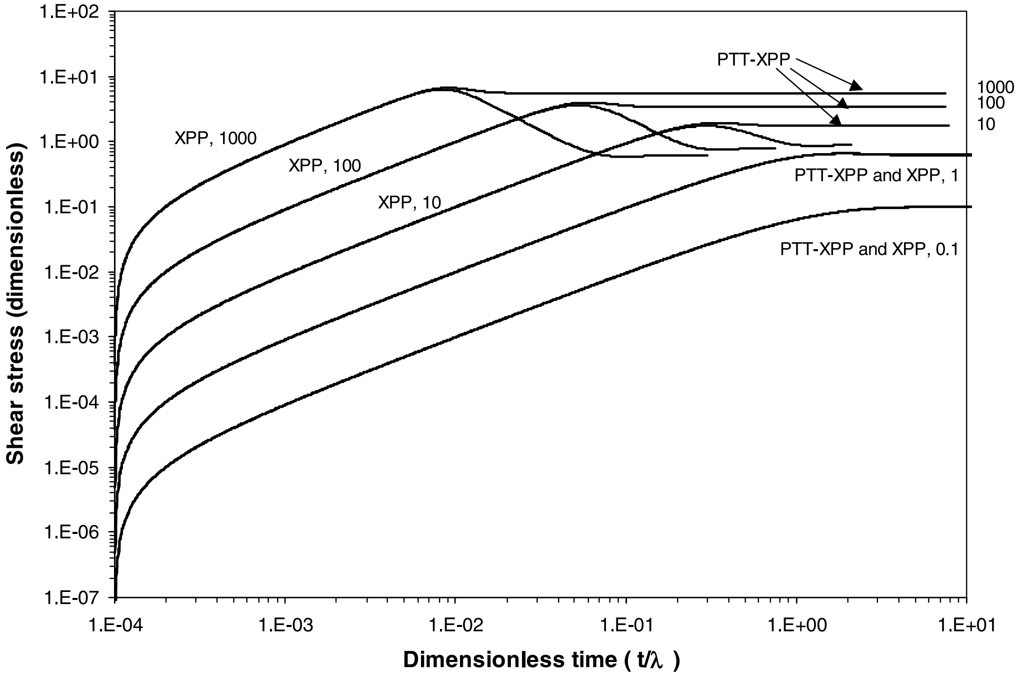

Fig. 9. The transient shear stress values for XPP and PTT–XPP models ($\nu = 1$, $r = 3$ and $\xi = 0$). Numbers attached to each model refer to the dimensionless shear rate value.

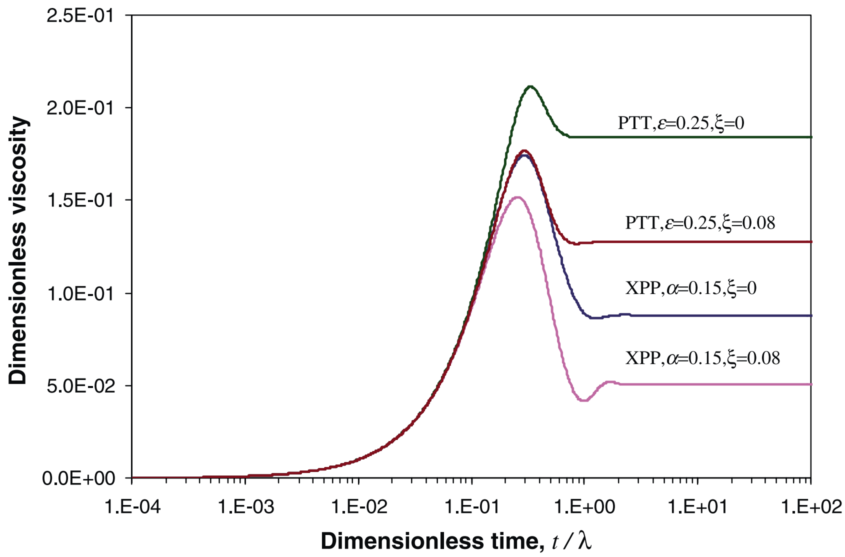

Fig. 10. Effect of slip factor ξ on transient response of XPP and PTT models at a dimensionless shear rate of 10 ($\nu = 1$, $r = 3$). α has an insignificant effect on the viscosity values of the XPP model.

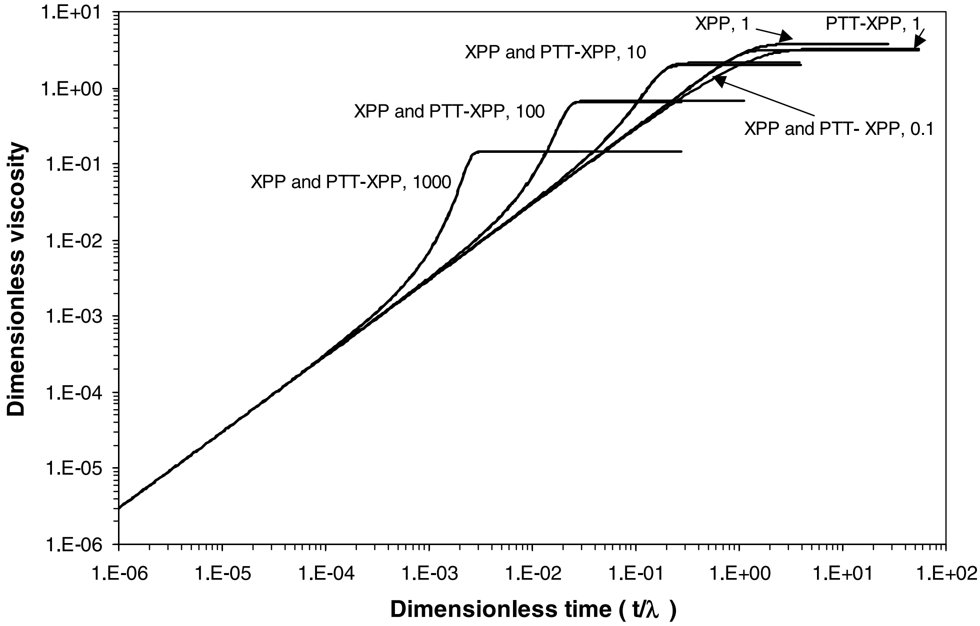

Fig. 11. The transient dimensionless viscosity values for of XPP and PTT–XPP models in elongational flow ($\nu = 1$, $r = 3$ and $\xi = 0$). Numbers attached to each model refer to the dimensionless strain rate value. Transient responses show no overshoot in elongation.

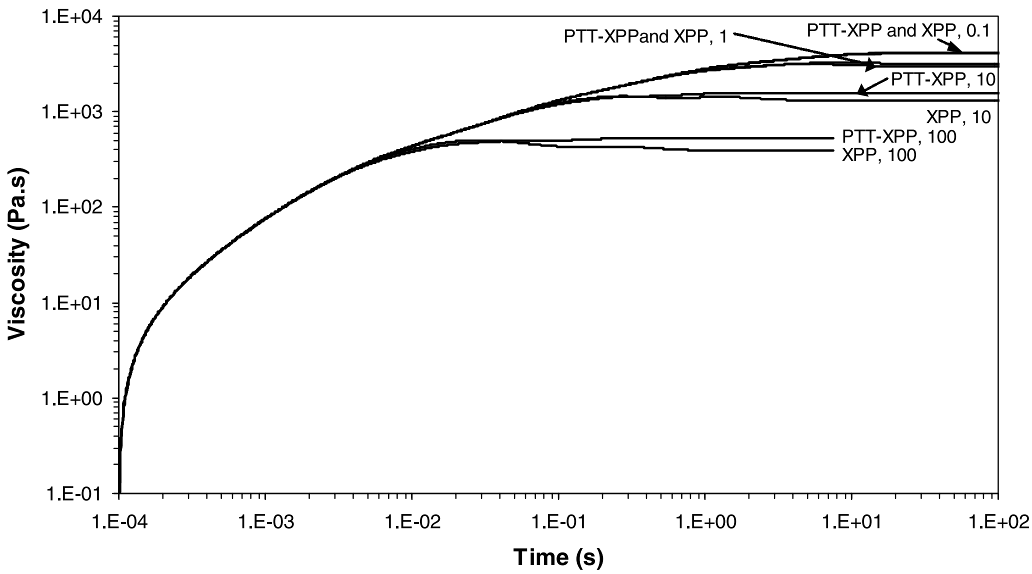

Fig. 12. Transient shear viscosity, for multi-mode XPP and multi-mode PTT–XPP models considering the values shown in Table 2. XPP results presented here are similar to the ones obtained by Verbeeten et al. [9] and the new PTT–XPP model predicts a shear viscosity very close to that of the XPP at each individual shear rate (attached to the model).

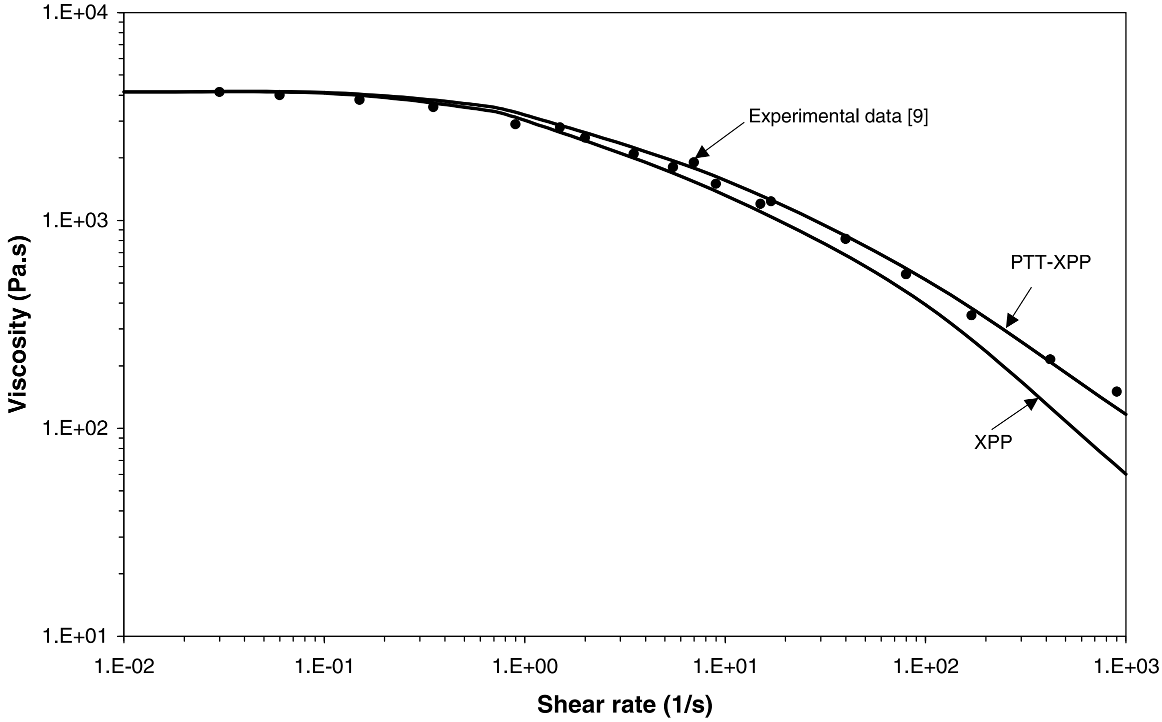

Fig. 13. Steady state shear viscosity, for multi-mode XPP (similar to the one obtained by Verbeeten et al. [9]) and multi-mode PTT–XPP model considering the parameters shown in Table 2. No attempt has been made to optimize the parameters for the PTT–XPP model, but results are very close to experimental values [9].

5. Conclusions

We have shown the similarity and difference of the responses of several simple single-mode constitutive models; these can, at least when put in multi-mode form, describe the behaviour of linear and branched polymers.

A new form of the single-mode PTT model (PTT–XPP) shows a nearly identical steady elongational response to the XPP model of Verbeeten et al. [6,9] (Fig. 1), but it differs from the XPP model at large shear rates (Fig. 2). Otherwise the behaviour of both is quite similar to the exponential PTT model, already in wide use. In shear flow, unlike the exponential PTT (with the slip parameter $\xi = 0$), the XPP model shear thins excessively (Fig. 2), so that a single-mode version of this model is statically unstable [10], with a maximum in the shear stress at $\lambda\dot{\gamma} \sim \mathrm{O}(10)$. It appears that the parameters r and ν are fitted and are not predictable a priori from molecular considerations.

Using the PTT–XPP and XPP models, one can investigate in a general way the effect of branching, via the ν parameter (Figs. 3–6). One of the problems to be faced in considering branched polymers is the fact that, except possibly for star polymers with equal arms, one does not know exactly what number and length of branches are present, which means that ν has to be inferred or fitted from rheological results. In any case, the single-mode concept is difficult to understand in a complex molecule, all modes are always present, so any finite number is an empirical approximation.

Finally, the biaxial and planar responses are shown for $\nu = 1$, $r = 3$ (Fig. 7). Transient responses show overshoots in shear (Figs. 8–10), but no overshoot in elongation (Fig. 11).

Clearly, since the Giesekus parameter α, has little effect, except to introduce N_2 into the viscometric flow, there is something to be said for using the simple PTT–XPP model.

Agreements have been obtained between the multi-mode models of XPP and PTT–XPP in elongational and shear flows and further parameter optimisation will decrease the small discrepancies between two models at high shear rates.

There are a number of points which can be made in using these single-mode elements in multi-mode fitting:

1. In elongation, there is a PTT model which will give results very close to the XPP model.
2. Usually, one should put the parameter $\xi = 0$, unless the second normal stress difference N_2 is important.
3. In shear, the PTT–XPP form will avoid the very rapid shear thinning occurring with XPP model; the XPP model is simply, in the single-mode form, unstable due to the maximum in the shear stress occurring at $\lambda\dot{\gamma} \sim \mathrm{O}(10)$.
4. The XPP and PTT models are seen to be two special cases of the general network model, with very similar types of network destruction functions, but with completely different network formation functions.
5. A flexible general network form can be found which enables elongational and shear results to be tailored to suit any given experimental data.
6. We believe the virtues of the general network model should be further explored.

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