Mesoscopic single and multi-mode rheological models for polymeric melts viscometric flows description

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Abstract: The Vinogradov and Pokrovskii rheological model was extended for a description of rheological behaviour of branched polymer melts. Since stationary elongational viscosity is a nonmonotonic function of the elongational rate, it required a generalization of the law of internal friction for beads of macromolecule. To achieve high prediction accuracy was proposed multi-mode approximation. The contribution of each independent mode to a stress tensor corresponds to the individual polymer fractions differing in relaxation time and viscosity. The theoretical predictions of the generalized model provide a good agreement with the measured steady and transient rheological characteristics of two samples branched low density polyethylenes.

Key–Words: Constitutive equations, Mesoscopic approach, Polymer dynamics, Polymer melts, Viscometric flows, Viscoelasticity

1 Introduction

The widespread introduction of polymers and products based on them in daily practice leads to increased attention to their production and processing. The demand of polymeric materials explains easy recycling as well as their unique properties, such as elasticity, strength, flexibility, good electrical insulation properties. Moreover, these properties cannot be explained only by the chemical composition of raw materials; the determining factor is chain structure of polymer molecules. It is well known that one of the important problems facing businesses is the issue of cost reduction in the production and processing. Effective solution to this problem is possible for optimizing technological processes, which it is impossible without building a mathematical model of behavior of polymeric media in different conditions of deformation. The work with such models is significantly complicated by the need to take into account non-linear effects and the effects of "memory" when considering the flow of polymer melts and fluids.

Thus a formulation of rheological constitutive relation, which establishes a connection between the kinematic characteristics of the flow and the internal thermodynamic parameters plays an important role when describing flows of solutions and melts of linear polymers in various modes of process equipment.

Experimental studies of various polymer liquids exhibit their nonlinear viscoelastic behavior. To describe these effects a large number of models that describe the rheological behavior of polymeric liquids, both qualitatively and quantitatively were proposed. It may be noted that there are two fundamentally different classes of models: in one case, a phenomenological approach is used, in the second takes microscopic approach. In the phenomenological approach, the dynamics of macroscopic bodies is built on the basis of general laws, which are found from experience. The phenomenological model of Maxwell, Oldroyd [1], Prokunin-Leonov [2] and others belong to this class of models. Another class of models is based on the mesoscopic approach [3-14]. In such models the dynamics of macromolecules should be described on the basis of model concepts and there-

fore takes into account a certain approximation, as the structure of the polymer molecules and processes of intermolecular interaction. Often in these models use single-molecule approach, in which instead of the entire set of macromolecules is considered one selected macromolecule, which moves in a "effective" environment. In some models of this class of macromolecule is often presented as a sequence of beads and connecting them springs (spring force); for example, one of the first of these models is Cargin-Slonimsky-Rouse model [3,4]. Thus, the mesoscopic approach, in contrast to the phenomenological, allows us to trace the connection between micro and macro properties of polymer systems. This helps to explain various phenomena in polymer melts, such as diffusion, viscoelasticity and others. However, introduction additional mesoscopic parameters that should be specified empirically is typical for such approach. These models include the Doi and Edwards[5] model, de Gennes[6], Curtiss and Bird[7]. In these models, each macromolecule is considered as a flexible chain, moving in a certain tube formed by other macromolecules; while for small molecule observation times can only make movements along the inside of the tube. However, the original model of Doi-Edwards does not take into account the elongation of each segment of the polymer chain. Subsequently model was modified to account for such extension. Generalization of the "reptation" is in [8], in which the dynamics of macromolecular chains examined on two dimensional levels - actually macromolecule and the level at which discusses the tube model. In [9] the one-chain problem for reptation and contour-length fluctuations which does not have any adjustable parameters was solved.

Another model [10], derived from the theory of "reptation", was developed to describe the dynamics of branched polymers, and a rheological model in differential form. It is based on the dynamics are not sequentially linked beads, but the beads are at the chain ends are connected to several. This is so-called pom-pom model. The disadvantage of this model is the zero value of the second normal stress difference in simple shear. Later, it was modified [11,12] and called the extended pom-pom model. These models consist of four differential equations containing an additional parameter that allows you to get a non-zero second normal stress difference with the shear flow. These models are system of differential equations containing an additional parameter that allows you to get a non-zero second normal stress difference with the shear flow. At present, various versions of the model "reptation" is most often used for the interpretation of experimental data in the study of the viscoelastic properties of solutions and melts. Nevertheless, the theoretical predictions are not always consistent with experi-

ments to quantify, although in general and give correct predictions. In some works, attempts to improve the agreement between theory experiments in quantitative terms, which leads to the theory of "double reptation", when taken into account local entanglements. Also, the presence of long chain macromolecular branching leads to additional difficulties when applying "reptation" model since in this case the "reptation" become impossible. In this case, the model should be improved; some studies specifically investigated macromolecular chains with long lateral branches. For example, in [8] has been shown that the presence of long chain branches per macromolecule leads to the appearance features of the viscoelastic behavior is especially important in processes involving polymer melts stretching.

In the case of the model Cargin-Slonimsky-Rouse or "beads-springs" generalization constructed to include consideration of "internal viscosity". It made it possible to describe the independence of the plateau modulus of the molecular weight of the polymer [13,14]. If thus consider only the slowest relaxation process in the polymer chain, it's possible to go to the model Vinogradov and Pokrovsky, and considering the induced anisotropy in the modified model Vinogradov and Pokrovsky [15-17]. It describes such effects observed in practice as the first and second normal stress difference, extensional viscosity increase, its output value on the other stationary and others. Furthermore, good correlation between theoretical and experimental curves of a wide range of deformation rates was observed.

The differential-vector-RHL model is also based on microstructure approach. In this model the dynamics of the macromolecule is described by the vector connecting the start and end of the polymer chain. This vector can be prolonged by increasing the length of the macromolecule, and also change the orientation by an external flow. RHL model is simple enough, but it was observed a good agreement this model with experimental data. In fact, this model makes it possible to consider the orientation of the chain and its extension separately with nonlinear elastic parameters of the coil macromolecule because it is based on the assumption that the orientation relaxation time longer relaxation time extension. At present, the development of new models still pays great attention to, for example, in [20], the authors try to solve the problem of describing the linear viscoelastic long-chain branched polymers. Besides, in [18, 19] the authors propose an advanced version of the MSF model allowing modeling of the transient and steady-state elongational viscosity data of monodisperse polystyrene melts without using any nonlinear parameter, i.e., solely based on the linear viscoelastic characteriza-

tion of the melts and then extend the same approach to model experimental data in shear flow.

Despite the large number of papers in the field of polymer media describe the dynamics of the most popular of these are: Prokunin and Leonov model [2], pom-pom model [10,11] and its modifications [12].

2 The rheological constitutive relation

To obtain rheological constitutive relation it is convenient to use the microstructural approach, which allows state a connection between the macro- and micro-characteristics of the polymer system [3-24]. Thus in the theory of viscoelasticity of the polymer the most productive is monomolecular approximation, when one selected macromolecule moving in an effective medium formed by the solvent and other macromolecules is considered instead of the totality of the macromolecules in the volume [13,14]. To investigate the relatively slow movements it is possible to use Kargin, Slonimskii, Rouse model [3,4] when dynamic equations of selected macromolecule are

$$m\frac{dr_i^\alpha}{dt} = -\zeta_{ij}(u_j^\alpha - \nu_{jk}r_k^\alpha) -$$
$$-2\mu T A_{\alpha\gamma}r_i^\gamma + \phi_i^\alpha(t), \qquad (1)$$
$$\alpha = 0, 1, 2, \ldots, N,$$

where m is the mass of a Brownian particle associated with a piece of the macromolecule of length M/N, r^α and $u^\alpha = \dot{r}^\alpha$ are the co-ordinates and velocity of the Brownian particle, ζ_{ij} - the tensor coefficient of friction and $2T\mu$ is the coefficient of elasticity of 'a spring' between adjacent particles, T is temperature in energy units. The matrix $A_{\alpha\gamma}$ depicts the connection of Brownian particles in the entire chain and has the form

$$A = \left\| \begin{array}{ccccc} 1 & -1 & 0 & \ldots & 0 \\ -1 & 2 & -1 & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & 0 & \ldots & 1 \end{array} \right\|.$$

The dissipative force in equations (1) are introduced by $\zeta_{ij}(u_j^\alpha - \nu_{jk}r_k^\alpha)$, presents the effective forces from the neighbouring macromolecules.

For the considered, linear in velocities, case, the correlation functions of the stochastic forces in the system of equations (1) can be easily determined from the requirement that, at equilibrium, the set of equations must lead to well-known results (the fluctuation-dissipation theorem). It is readily seen that, according

to the general rule [8,14],

$$\langle \phi_i^\alpha(t)\phi_k^\gamma(t')\rangle = T\zeta_{ik}\exp\left(-\frac{t-t'}{\tau}\right). \qquad (2)$$

It should be mentioned that such an approach leads to rheological defining relations of varying degrees of complexity, a review of papers in this direction and comparison with other approaches can be found in [14]. The simplest of them basic rheological model [15,16], allows modeling steady viscometric flow of solutions and melts of linear polymers, not only qualitatively but also quantitatively. Therefore it is necessary to consider this model in more detail. In this case it is possible to model the dynamics of macromolecules on elastic dumbbell ($N = 2$), which corresponds to the consideration of the only one (the slowest), relaxation process of the polymer chain. In the inertialess case in the laboratory system the equation of dynamics of macromolecules (1) will take the following form

$$\dot{r}_i^2 = \nu_{ij}r_j^2 - 2T\mu\zeta_{ij}^{-1}(r_j^2 - r_j^1) + \zeta_{ij}^{-1}\phi_j^2, \qquad (3)$$
$$\dot{r}_i^1 = \nu_{ij}r_j^1 - 2T\mu\zeta_{ij}^{-1}(r_j^1 - r_j^2) + \zeta_{ij}^{-1}\phi_j^1.$$

If the anisotropy of the considered polymer system is determined by a symmetric second-rank tensor a_{ij}, then for the friction tensor ζ_{ij} the following expressions should be used [25,26]

$$\zeta_{ij} = B\zeta\left(\delta_{ij} + 3\beta\left(a_{ij} - \frac{a_{jj}}{3}\delta_{ij}\right) + \kappa a_{jj}\delta_{ij}\right)^{-1},$$

$$(4)$$

where ζ - the coefficient of friction of the beads in the "monomer" liquid (for spherical particles $\zeta = 6\pi R\eta_s$); B - measure of the friction coefficient gain; and β, κ - scalar coefficients of anisotropy taking into account the isotropic and anisotropic contributions to the dependence respectively ζ_{ij} from a_{ij}. The expression (4) was obtained previously as a self-consistent generalization to the case of large deformations of expression [15]:

$$\zeta_{ij} = B\zeta\left(\delta_{ij} - 3\beta\left(a_{ij} - \frac{a_{jj}}{3}\delta_{ij}\right) - \kappa a_{jj}\delta_{ij}\right).$$

The above dynamic equations were designed [23] to describe effects in entangled systems, that is in the systems consisting of macromolecules of length $M > 2M_e$, where M_e is the length of the macromolecule between adjacent entanglements [21]. In the case, when $\zeta_{ik} = \zeta\delta_{ik}$, the considered equations

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describe the Rouse dynamics of macromolecule in a viscous liquid [3]. For entangled systems in [13-16] are introduced measures of intensities of the external and internal extra dissipative forces in Eq. 1, connected with the neighbouring macromolecules. The dependence of the quantity B on the length of macromolecules can be estimated [13] by using simple picture of overlapping coils [24] or the constraint-release mechanism [22].

The meaning of this expression corresponds with the notion that for a small deformation of the polymer system it is more convenient to change its shape in the direction determined by the tensor a_{ij}, which leads to reducing the friction. It is clear that for large deformations this relation will become incorrect (the value of the friction tensor can be negative). Therefore, expression (4) was proposed. However, this generalization does not include all the features of the processes at large deformations. It is a more realistic situation when parameters β and κ themselves depend on the anisotropy tensor and its invariants. The preliminary investigation showed that β and κ have to be slowly increasing functions of the first invariant of the tensor anisotrophy a_{ij}. Further consider the situation where as such dependence expressions of the form are used

$$\beta(I) = \frac{\beta_0 + pI}{1 + pI}, \kappa(I) = \frac{\kappa_0 + pI}{1 + pI}, I = a_{jj}. \quad (5)$$

Here β_0 and κ_0 - initial values of anisotropy parameters, p - parameter takes account of the effect of the first invariant I on $\beta(I)$ and $\kappa(I)$.

It is now possible to obtain the rheological constitutive relation. When deducing it's convenient to go to new coordinates by means of

$$\rho_i = \frac{1}{\sqrt{2}}(r_i^1 - r_i^2), \qquad \rho_i^0 = \frac{1}{\sqrt{2}}(r_i^1 + r_i^2). \quad (6)$$

Coordinate ρ_i^0 describes movement of the gravity center of the dumbbell, and ρ_i - relative movement of the beads. Then equations (3) in coordinates (6) take the form

$$\dot{\rho}_i = \nu_{ij}\rho_j - 4T\mu\zeta_{ij}^{-1} + \frac{1}{\sqrt{2}}(\phi_i^1 - \phi_i^2),$$

$$\dot{\rho}_i^0 = \nu_{ij}\rho_j^0 + \frac{1}{\sqrt{2}}(\phi_i^1 + \phi_i^2).$$

Now receive the equations for the correlation moment $m_{ik}(t) = \langle \rho_i(t)\rho_k(t) \rangle$, where the averaging procedure is performed over all possible realizations of random forces. Differentiating $m_{ik}(t)$ on time and using the recently ratio, we obtain

$$\frac{d}{dt}m_{ik} = \nu_{ij}m_{jk} + \nu_{kj}m_{ji} -$$
$$-4T\mu\zeta_{ij}^{-1}m_{jk} - 4T\mu\zeta_{kj}^{-1}m_{ji} + \quad (7)$$
$$+\frac{1}{\sqrt{2}}\langle\left(\phi_i^1 + \phi_i^2\right)\rho_k\rangle\frac{1}{\sqrt{2}}\langle\left(\phi_k^1 + \phi_k^2\right)\rho_i\rangle.$$

Correlation moments $\langle\left(\phi_i^1 + \phi_i^2\right)\rho_k\rangle$ which are unknown in (7) can be found from the corresponding fluctuation-dissipation relation (2), but its possible to do otherwise. Note that the equilibrium (when $\nu_{ik} = 0$) value of correlation moment m_{ik} was defined previously [12,13,23] ($m_{ik}^0 = \delta_{ik}/4\mu$). Besides equations (7) are linear with respect to m_{ik}, so the influence of moment $\langle\left(\phi_i^1 + \phi_i^2\right)\rho_k\rangle$ means that it is necessary to replace m_{ik} on $m_{ik} - m_{ik}^0$ everywhere whan m_{ik} has no factor of velocity gradient tensor ν_{ik}. Then instead of (7) we obtain

$$\frac{d}{dt}m_{ik} = \nu_{ij}m_{jk} + \nu_{kj}m_{ji} - \quad (8)$$

$$-4T\mu\zeta_{ij}^{-1}\left(m_{jk} - \frac{1}{4\mu}\delta_{jk}\right) -$$

$$-4T\mu\zeta_{kj}^{-1}\left(m_{ji} - \frac{1}{4\mu}\delta_{ji}\right).$$

Now note that tensor m_{ik} describes the shape and size of the macromolecular coil. And since the anisotropic properties of polymer media are determined by the size and shape of the macromolecular coils, the anisotropy tensor, which describes the deviation of the statistically nonequilibrium system from equilibrium can be defined as

$$a_{ik} = \frac{\langle\rho_i\rho_k\rangle}{\langle\rho^2\rangle_{eq}} - \frac{1}{3}\delta_{ik} = \frac{4\mu}{3}m_{ik} - \frac{1}{3}\delta_{ik}. \quad (9)$$

Then using (9), equations (8) can be rewritten as

$$\frac{d}{dt}a_{ik} - \nu_{ij}a_{jk} - \nu_{kj}a_{ji} +$$

$$+\frac{1 + (\kappa - \beta)I}{\tau_0}a_{ik} = \frac{2}{3}\gamma_{ik} - \frac{3\beta}{\tau_0}a_{ij}a_{jk}, \quad (10)$$

where $\tau_0 = \zeta/(8T\mu)$ - initial relaxation time; $\gamma_{ik} = (\nu_{ik} + \nu_{ki})/2$ - symmetrized velocity gradient tensor.

For comparison (10) with experimental data the expression for the stress tensor of the polymer system is required. It can be obtained in a standard way [14-16] and in generalized coordinates (5) has the form

$$\sigma_{ik} = -2nT\delta_{ik} + 4nT\mu\langle\rho_i\rho_k\rangle.$$

Where n - number of macromolecules in init volume. Using notation (9), the last expression can be written as

$$\sigma_{ik} = -\hat{p}\delta_{ik} + 3\frac{\eta_0}{\tau_0}a_{ik}, \qquad (11)$$

where $\hat{p} = nT$ - hydrostatic pressure; $\eta_0 = nT\tau_0$ - initial value of the shear viscosity.

Thus, (4), (10), (11) form a rheological constitutive relation of the nonlinear anisotropic viscoelastic fluid with parameters: η_0, τ_0, κ and β, which in turn have to depend on the molecular weight of polymer M and its concentration c . For example, the dimensional parameters can be estimated by formulas [24-26]:

$$\eta_0 = \eta_0(c^*, M^*)\left(\frac{c}{c^*}\right)^{4,5} \cdot \left(\frac{M}{M^*}\right)^{3,4}, \tau_0 = \frac{\eta_0}{nT},$$

where M^*, c^* - some fixed values of molecular weight and concentration at which the initial values of viscosity and relaxation time are known.

As for the parameters of the induced anisotropy κ_0, β_0 and p, there is a reason to assume that for linear polymers, they do not depend on the molecular weight or the concentration of [26,27,28].

3 Non-linear effects in simple shear and uniaxial elongation

The rheological constitutive relation (10), (11) obtained above needs to be checked for compliance with the flow of real polymeric liquids. Flows realized in experiments with solutions and melts of linear polymers, are very diverse: stationary and non-stationary, linear and non-linear, homogeneous and heterogeneous. It is clear that any check on the adequacy of the rheological model should start with the simplest flows. It should also be noted that the calculation of the most complex flows - heterogeneous stationary and non-stationary (when it is necessary to determine the velocity field of polymer liquid and a velocity gradient tensor) - are very time-consuming, even for fairly simple models and require using numerical methods for solving partial differential equations. Therefore such calculations are quite a complex mathematical problem [26-29].

At the beginning consider viscosimetric flows of polymer media. Such flows are implemented in viscometers of different designs, and they are characterized by the fact that the velocity gradient tensor is a known function of time. Therefore, modeling such flows is reduced to the integration of ordinary differential equations for the internal thermodynamic parameters, which is an easy task.

Simple shear and uniaxial elongation are the most investigated viscometric flows. In the case of a simple shear flow, where only one component of velocity gradient tensor $\nu_{12}(t)$ is different from zero, rheological behavior of the polymer system is characterized by the following viscometric functions: shear stress - σ_{12} ; shear viscosity - η ; first normal stress difference - N_1 and second normal stress difference - N_2, which are determined as:

$$\eta = \frac{\sigma_{12}}{\nu_{12}}, N_1 = \sigma_{11} - \sigma_{22}, N_2 = \sigma_{22} - \sigma_{33}, \quad (12)$$

and in general they are functions of the shear rate γ and time t.

If the function of shear rate on the time given as $\nu_{12}(t) = \gamma E(t)$ or $\nu_{12}(t) = \gamma E(-t)$, where $E(t)$ - Heaviside unit function, than the first case describes establishment of shear stress from the steady state, and second - the stress relaxation after shear deformation. Then viscosimetric functions (13) are denoted $\eta^+(\gamma, t)$, $N_1^+(\gamma, t)$ and $\eta^-(\gamma, t)$, $N_1^-(\gamma, t)$ respectively.

Also of interest are the stationary values of $\eta^+(\gamma, t)$, $N_1^+(\gamma, t)$:

$$\eta(\gamma) = \lim_{t\to\infty} \eta^+(\gamma, t), \; N_1(\gamma) = \lim_{t\to\infty} N_1^+(\gamma, t). \; (13)$$

Sometimes it is convenient to consider various combinations of variables introduced into consideration, for example

$$\Psi_1(\gamma) = \frac{N_1}{\gamma^2}, \; \Psi_2(\gamma) = \frac{N_2}{\gamma^2}. \qquad (14)$$

Here Ψ_1 and Ψ_2 - coefficients of the first and second normal stress difference.

Numerous experimental data on the shear deformation of solutions and melts of linear polymers show that shear viscosity - is a decreasing function of shear rate; shear stress $\eta(\gamma)$ is an increasing function of shear rate; Ψ_1 and Ψ_2 - coefficients of the first and second normal stress difference are decreasing functions of shear rate; ratio of the second normal stress difference to the first is a small quantity, which dependence on the shear rate is not enough investigated in experiments [30].

In the case of uniaxial tension, when only the diagonal terms of the tensor of velocity gradients are

different from zero $\nu_{11} = -\nu_{22} = -|nu_{33} = \gamma$, rheological behavior of the polymer fluid has a viscosity in uniaxial elongation - λ, defined as

$$\lambda(\gamma) = \frac{\sigma_{11} - \sigma_{22}}{\gamma}. \qquad (15)$$

Viscosity in tension can be both increasing and decreasing function of strain rate. More detailed information about the behavior of viscometric functions are given below when comparing detected theoretical dependencies with the experiments described in literature. The resulting equations require a numerical solution. When considering non-linear effects in steady shear flow system (10), (11) takes the following form

$$a_{11} = 2\tau_N s a_{12} - 3\beta(I)\tau_N(a_{11}^2 + a_{12}^2), \qquad (16)$$
$$a_{22} = -3\beta(I)\tau_N(a_{22}^2 + a_{12}^2),$$
$$a_{12} = \frac{\tau_N}{3} + \tau_N s a_{22} - 3\beta(I)\tau_N a_{12}(a_{11} + a_{12}).$$

Here $\tau_N = 1/(1 + \kappa(I) - \beta(I))I$, $I = a_{11} + a_{12}$, $s = \tau_0\gamma$.

The calculation results of viscometric functions (13), (14) on the basis of the system of equations (17) are shown in Figures 1-6. Figures 1,2 shows the dependence steady shear viscosity η of dimensionless shear rate s. Stationary shear viscosity is a decreasing function of shear rate. Thus with increasing β_0 the deviation of the initial value of steady shear viscosity increases, too.

Figures 5,6 shows the ratio of the second normal stress difference to the first defined by (14). This ratio is less than zero and small in absolute value. The parameter β_0 affects on the ratio significantly, whereas κ_0 - insignificantly. Also influences the coefficient of the first normal stress difference Ψ_1, shown in Figures 3,4. All these calculations are in good agreement with the experimental data.

In the case of uniaxial tension stationary system of equations (10) and (11) takes the following form

$$3\beta(I)\tau_N s b_{11}^2 + (1 - 2\tau_N s)b_{11} = \frac{2}{3}\tau_N s, \qquad (17)$$

$$3\beta(I)\tau_N s b_{22}^2 + (1 + \tau_N s)b_{22} = \frac{1}{3}\tau_N,$$

where $I = (b_{11} + 2B_{22})s$, $s = \tau_0\nu_{11}$ and $b_{ii} = a_{ii}/s$.

In this case, the behavior of the polymer is characterized by a stationary elongation viscosity (15), which dependencies of the dimensionless elongation rate for various parameter values κ_0, β_0 and are shown in Figure 7. At high tension rates $\lambda(s)$ becomes constant ($\lambda_\infty \sim 1/\beta_0$), if $p = 0$. When p is
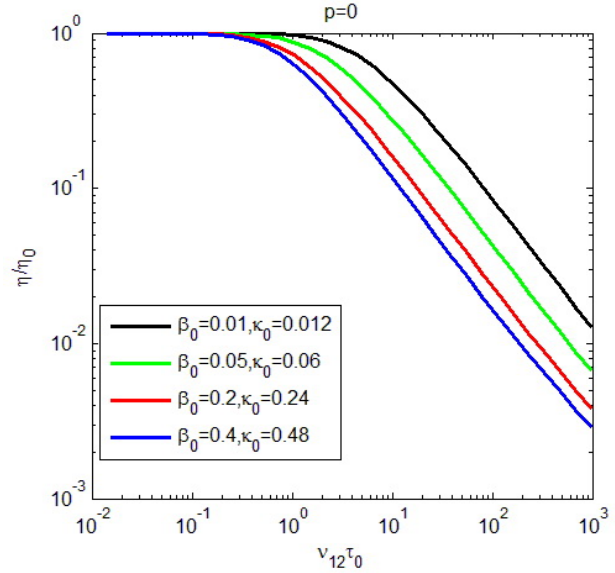

Figure 1: Steady shear viscosity coefficient as a function of dimensionless shear rate s for $p = 0$ and different parameter values κ_0, β_0.
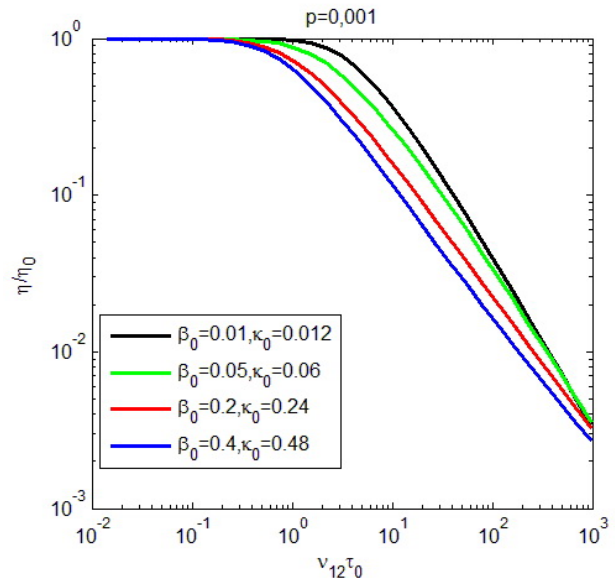

Figure 2: Steady shear viscosity coefficient as a function of dimensionless shear rate s for $p = 0.001$ and different parameter values κ_0, β_0.
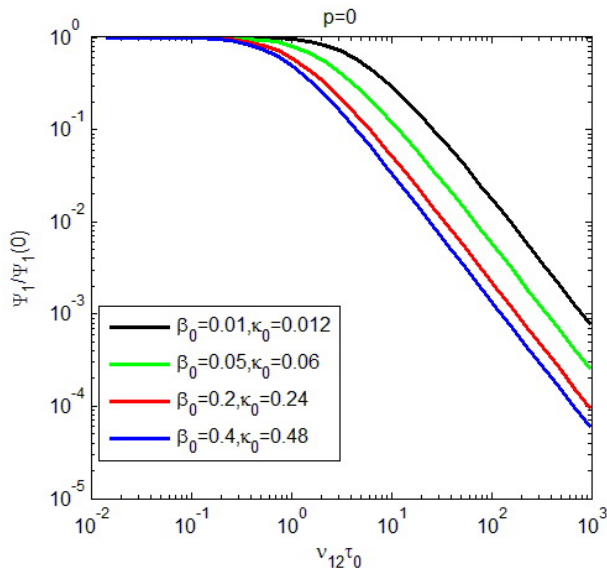
Figure 3: Coefficient of the first normal stress difference as a function of dimensionless shear rate s for $p = 0$ and different parameter values κ_0, β_0.
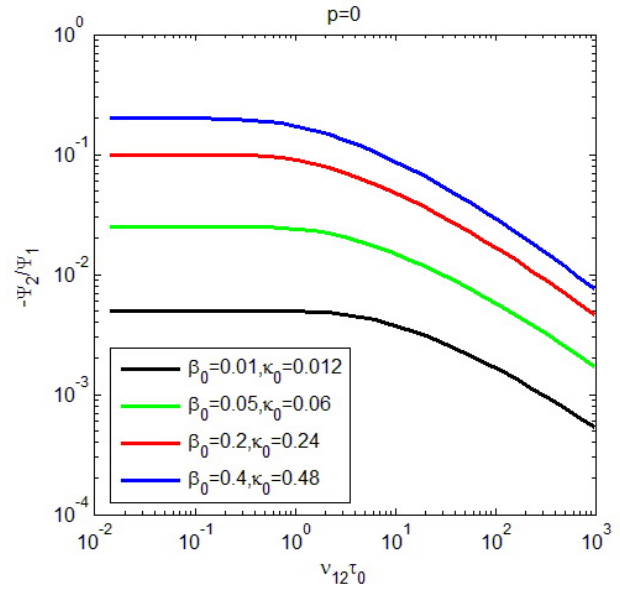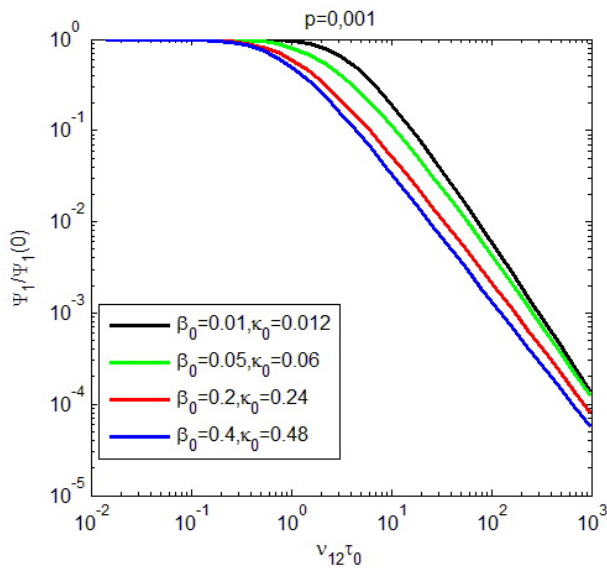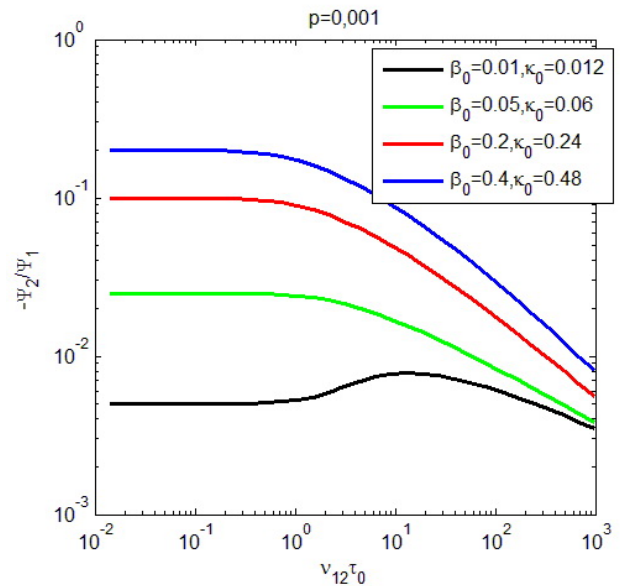

Figure 5: The ratio of the second normal stress difference to the first as a function of dimensionless shear rate s for $p = 0$ and different parameter values κ_0, β_0.
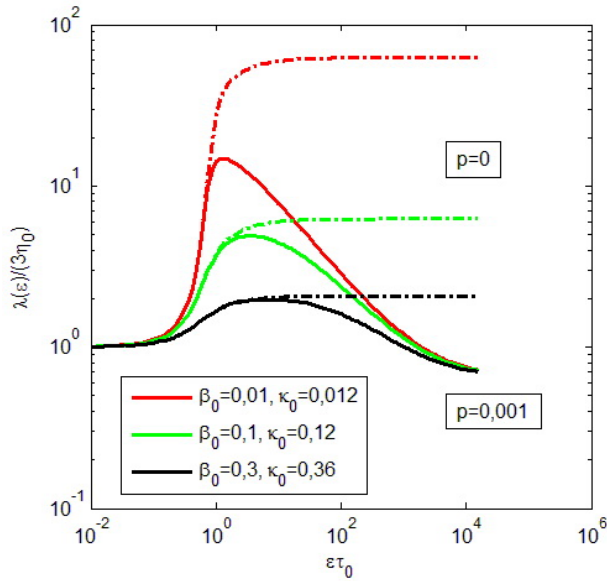

Figure 4: Coefficient of the first normal stress difference as a function of dimensionless shear rate s for $p = 0$ and different parameter values κ_0, β_0.

Figure 6: The ratio of the second normal stress difference to the first as a function of dimensionless shear rate s for $p = 0$ and different parameter values κ_0, β_0.

Figure 7: Dependence of the steady state elongation viscosity coefficient λ of dimensionless elongation rate s for different parameter values κ_0, β_0 and p.

Figure 8: Establishment of simple shear viscosity.

different from zero dependence of viscosity in tension goes through a maximum. This corresponds to calculations based on similar rheological models, such as Prokunin-Leonov model [2] or pom-pom model [10-12].

Obtained non-linear systems of algebraic equations (16) and (17) were solved with the method of sequential approximations and a modified Newton's method, and then the solutions are compared with each other.

Shown in Figures 1-7 dependencies demonstrate qualitative accordance of the model (10), (11) to the actual behavior of solutions and melts of linear polymers in the flow. Most often stady state shear viscosity coefficient η and first normal stress difference N_1 are investigated in experiments. By choosing parameters η_0, τ_0, κ_0, β_0 and p it's possible to describe dependences $\eta(\nu_{12})$ and $N_1(\nu_{12})$ for some values of molecular weight M and concentration c of polymer quite accurately. Therefore, the greatest interest is the problem of describing a series of experiments on steady simple shear for the given polymer at a different values M and c. The solution of this problem can be found in [26,27] for the case $(p = 0)$, which shows the applicability of a rheological model (10), (11) to describe the steady shear flow solutions and melts of linear polymers in a wide range of shear rates. Also, it is established that in the description of the dynamics of linear polymer model parameters κ_0 and β_0 are weakly dependent on the molecular weight and concentration, which can be the basis for consideration in
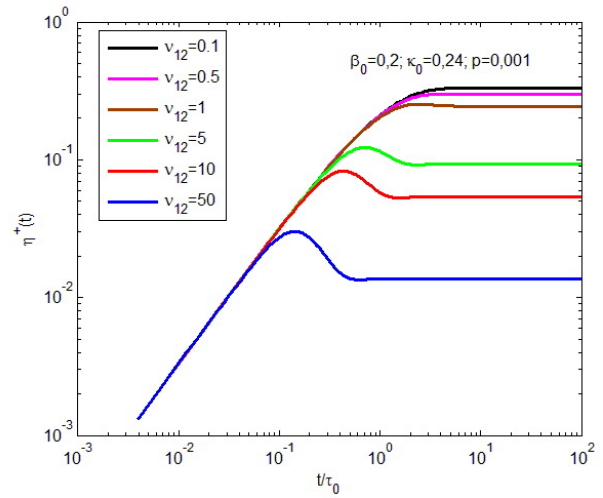
this model, the effects associated with polydispersity of the polymer material.

Now let us consider unsteady effects on the basis of the rheological model (10), (11). To do this we consider the problem of establishment stresses in simple shear, after instant application of shear deformation at a constant shear rate ν_{12} . It is convenient so because it is possible to compare the results obtained, both with the experimental data [30] and with calculations based on other models [2,10-12].

The calculation of viscometric functions (13-15) for the system (10), (11) is carry out. In this case, the equation for the non-zero components of anisotropy tensor takes the following form

$$\frac{d}{dt}a_{11} - 2\gamma_{12} + \frac{1 + (\kappa - \beta)I}{\tau_0}a_{11} = -\frac{3}{\tau_0}\beta(a_{11}^2 + a_{12}^2),$$

$$\frac{d}{dt}a_{12} - \gamma_{22} + \frac{1 + (\kappa - \beta)I}{\tau_0}a_{12} =$$
$$= \frac{1}{3} - \frac{3}{\tau_0}\beta a_{12}I, \qquad (18)$$

$$\frac{d}{dt}a_{22} + \frac{1 + (\kappa - \beta)I}{\tau_0}a_{22} = -\frac{3}{\tau_0}\beta(a_{22}^2 + a_{12}^2),$$

Since the deformation starts from the steady state, the system of differential equations (18) should be solved with the initial conditions $a_{ij}(0) = 0$. Numerical calculations of the system (18) were produced by Runge-Kutt method with fourth-order accuracy.

We can construct establishment viscosity in shear and uniaxial tension following similar actions. The calculated dependences are given in Figures 8 and
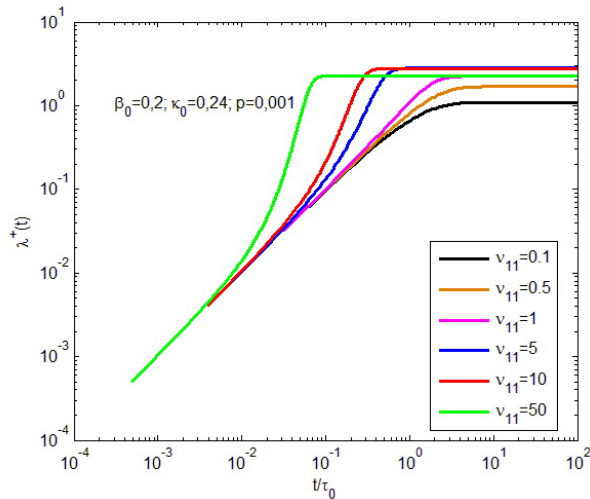
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Figure 9: Establishment stresses in uniaxial elongation.

Figure 10: Comparison of experimental [30] and theoretical dependences to establish shear viscosity and elongation viscosity for single-mode model.

9. In the case of a simple shear we are seeing non-monotonic output of viscosity on steady-state value (Figure 8). And in the case of a uniaxial elongation - monotonic output of viscosity on steady-state value (Figure 9).

Thus, the model (10), (11) can be chosen as the initial approximation in the description of nonlinear and viscoelastic properties of solutions and melts of linear and branched polymers. The obtained results only qualitatively coincide with experimental data presented in [27,28] and shown in Figure 10. The calculation results, despite the simplicity of the system (10), (11) or (18), predicts non-monotonic stress setting $\sigma_{12}(\gamma t)$ acceptable values for in the middle range of values γ and time t.

Analyzing the above we should not expect that the system of equations (10) and (11) will be fully adequate to the real data because only single relaxation process was taken into account. Also, the system of equations (10), (11) does not allow to describe the dependence of the dynamic shear modulus on frequency [24]. Therefore the further study of the rheological model that takes into account the multiplicity of relaxation times is of great interest.

4 Multi-mode rheological model

The multi-mode character of dynamics of polymeric fluids or multiplicity of relaxation processes is apparent already in the case of analysis for monodisperse polymer solutions with flexible chains [13, 24]. This is first of all connected with topology of branched polymer molecules. Obtained relaxation times in dependence on a mode number exhibit vanishing
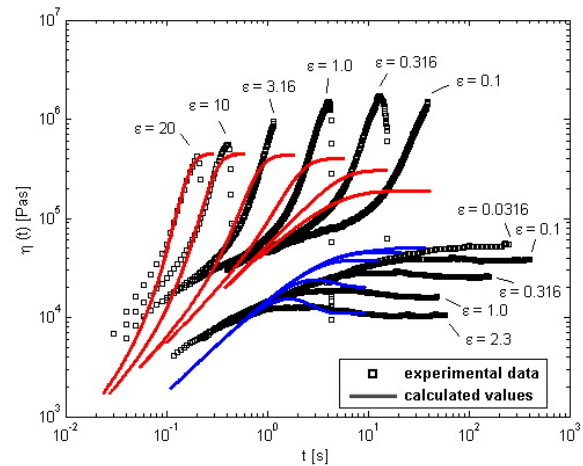
behaviour inversely proportional to the mode number, in other words so-called Rouse character. Increase in concentration of polymer in a system results in macromolecular entanglements, the dynamics becomes more complex, long-scale interrelations originate between the macromolecular parts. This is reflected in the additional components in the corresponding stress tensor of a polymeric system or in respect to new relaxation processes with relatively low time relaxations [16]. The rheological relations obtained in these papers sufficiently describe the relations of linear viscoelasticity, dependence of storage and loss moduli on frequency. A description of nonlinear behaviour represents another important problem in the dynamics of polymeric fluids.

It is apparent that in the case of materials exhibiting polydispersity or branched topology, multiplicity of relaxation processes plays still a more important role. In this case the behaviour of the characteristics of relaxation process (its relaxation time and its participation in stress tensor) has no longer the Rouse character and generation is necessary.

Regardless of this, for a description of dynamics of concentrated polymeric systems, a perspective rheological model should be proposed based on a mesoscopic approach. This approach taking into account a description of comparatively slow heat macromolecular movement uses such model representations as e.g. a dashpot-spring model. Apart from Rouse parameters (friction coefficient of a dashpot, equilibrium dimension of macromolecular coil, etc.), the additional parameters are necessary to be included in the description of concentrated systems correspond the nature of entanglement in the concentrated poly-

meric systems. In this sense we will use the modified Vinogradov-Pokrovskii model [25-30]. An advantage of this model is respecting a tensor character of friction coefficient of the dashpots related with supposed anisotropy of shear flow. Such anisotropy is determined by the dimensions and form of a macromolecular coil which reflects additional parameters in the equations of motion. The generalisation of this model to a multi-mode case proposed in [28,29] is of the following form

$$\sigma_{ik} = -\hat{p}\delta_{ik} + 3\sum_{\alpha=1}^{n} \frac{\eta_\alpha}{\tau_\alpha} a_{ik}^\alpha, \qquad (19)$$

$$\frac{d}{dt}a_{ik}^\alpha - \nu_{ij}a_{jk}^\alpha - \nu_{kj}a_{ji}^\alpha + \frac{1 + (\kappa_\alpha - \beta_\alpha)a_{jj}^\alpha}{\tau_\alpha}a_{ik}^\alpha =$$

$$= \frac{2}{3}\gamma_{ik} - \frac{3\beta}{\tau_\alpha}a_{ij}^\alpha a_{jk}^\alpha,$$

where $\hat{p}$ is hydrostatic pressure, σ_{ik} is the stress tensor, ν_{ij} is the velosity gradient tensor, γ_{ik} is the symmetrical part of velosity gradient tensor, α is the mode number, n is a number of relaxation modes or processes, a_{ik}^α is the dimensionless extra stress tensor corresponding to α mode, η_α is the coefficient of shear viscosity of α mode, τ_α is the relaxation time of α mode, $\kappa_\alpha = \kappa_\alpha(a_{jj}^\alpha)$ and $\beta_\alpha = \beta_\alpha(a_{jj}^\alpha)$ are the parameters of the suggested anisotropy given by the functions

$$\beta_\alpha(a_{jj}^\alpha) = \frac{f_\alpha + p_\alpha a_{jj}^\alpha}{1 + p_\alpha a_{jj}^\alpha},$$
$$\kappa_\alpha(a_{jj}^\alpha) = 1, 2 \cdot \beta_\alpha(a_{jj}^\alpha). \qquad (20)$$

The equations presented in [23,24] are first formulated in a multi-mode approximation and consequently simplified. While deriving the relations (20) it was supposed that the parameters of the suggested anisotropy do not depend or depend negligibly on a number of modes. However, the comparison with the experimental data proved this assumption wrong. Hence, it is necessary to return to the multi-mode approximation. It is expected that an application of more relaxation modes will improve the description of the materials used and agreement with the experimental data.

Influence of the parameters of the suggested anisotropy is different for each mode. Therefore, it is useful to investigate each mode separately as given by the formulation of the expressions (20). For setting there was used the relation $\kappa_\alpha(a_{jj}^\alpha) = 1, 2 \cdot \beta_\alpha(a_{jj}^\alpha)$ was used as proposed in [25].

Hence, in the set of equations (19,20) parameters $\eta_\alpha, \tau_\alpha, p_\alpha$ and f_α are only unknowns and should be determined by means of the experimental data. A number of these parameters are not low, especially with an increasing number of the modes. Therefore, it is necessary to present their determination more carefully.

5 Determination of the parameters for multi-mode rheological model

It is obvious that the accuracy between a theoretical prediction and the experimental data represents a crucial factor for choosing an adequate rheological model. It is feasible to use such different materials with the values of some parameters close and others are different. Such comparison for two different polymer melts is presented in [29,30].The determining relations were obtained using the experimental data in [30] presented the rheological characteristics of two highly-branched polyethylenes of low density, namely LDPE Bralen RB0323 (Slovnaft, Slovakia) and LDPE Escorene LD165BW1 (Exxon, USA). The experiments were carried out at the temperature of 200^oC. In the paper [30] storage and loss moduli were measured by different procedures, a determination of stresses, transient and steady behaviour of shear viscosity and the coefficient of the first normal stress difference. Capillary rheometer RH7 (Rosand Precision) was used for a determination of rheological characteristics under high shear rates. The coefficient of the first normal stress difference was determined using a slit geometry. A uniaxial elongational viscosity was measured using the SER Universal Testing Platform (Xpansion Instruments, USA) housed in the ARES 2000 rheometer (TA Instruments, Germany). The experimental details are presented in [30].

First, it is necessary to determine parameters and with the dimensions of viscosity and time, respectively. If we solve the second equation of the set (19) with the accuracy up to the components of the first order with respect to the velocity gradient, we obtain

$$\frac{d}{dt}a_{jk}^\alpha + \frac{1}{\tau_\alpha}a_{jk}^\alpha = \frac{2}{3}\gamma_{ik}$$

This equation coincides with Maxwell equation and its usage provides the relations of linear viscoelasticity. From here and from (19) we get the relations for determination of storage moduli $G'(\omega)$ and loss moduli $G''(\omega)$ which can be obtained easily [1,2,22]

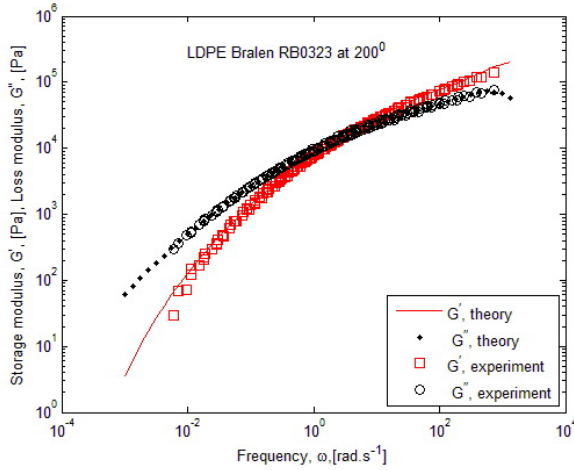$$G'(\omega) = \sum_{\alpha=1}^{n} \frac{\omega^2 \tau_\alpha \eta_\alpha}{1 + (\omega\tau_\alpha)^2},$$

Figure 11: Comparison of the shear and loss moduli vs. frequency dependence with the experimental data for Bralen [30].

Figure 12: Comparison of the shear and loss moduli vs. frequency dependence with the experimental data for Escorene [30].

$$G''(\omega) = \sum_{\alpha=1}^{n} \frac{\omega \eta_\alpha}{1 + (\omega \tau_\alpha)^2}. \qquad (21)$$

These relations coincide with the results presented in other rheological models [29,30,33,34]. The procedure of determination of η_α and τ_α is based on least-square minimization.

The values of the moduli calculated according to (21) can be compared with the experimental data. The calculations were carried out for 10 modes and the values of the parameters obtained by an optimization procedure between the calculations and the experiments given in Table 1. Relaxation spectra were calculated in [30] from the loss and storage moduli by the help of the generalized Maxwell model. The values of viscosity parameter η_α were determined with the help of relation: $\eta_\alpha = g_\alpha \tau_\alpha$. The fitting curves of the generalized Maxwell model for both described materials are shown in Figures 11,12.

To determine the values of the parameters of anisotropy in the paper [30] contributions of each mode and the values of f_α and p_α were determined at each part of steady viscosity dependence under uniaxial elongation. From here it followed that both f_α and p_α are non-monotonous functions of mode number α. At the beginning the values of these parameters are increasing with increasing α, then they are decreasing. They attain their maxima for $\alpha = \alpha_0$. Hence, in the following we will approximate these parameters by the expressions

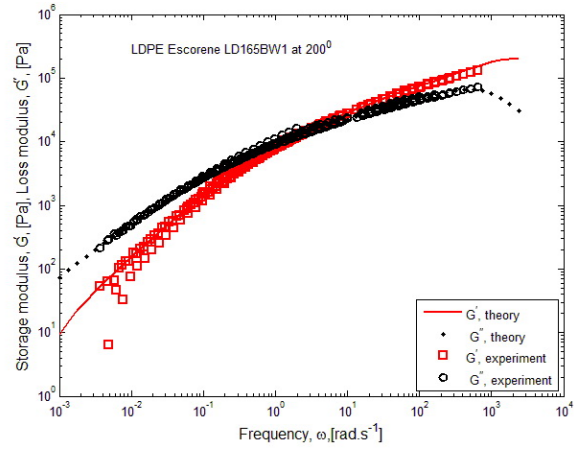$$f_\alpha = \frac{B}{1 + (\alpha - \alpha_0)^2}, \qquad p_\alpha = \frac{P}{1 + (\alpha - \alpha_0)^2}. \quad (22)$$

Let us analyses these relations in more detail. A mode denoted by α_0 corresponds to a mean value of molecular weight M_n. It is possible to expect that a shape and size of a macromolecular coil corresponding to M_n will exhibit the highest influence on the dynamics of polymer liquid. The fractions which molecular weight apparently differs from M_n have negligible impact on nonlinear viscoelastic properties of such a system. It implies that for $\alpha \to \infty$ the parameters f_α and p_α will attain infinitely low values. Naturally, in reality this limited passage is not possible to put into effect, however, when the difference between mode numbers attain 5 then their influence attenuates 25 times.

6 Viscometric functions for simple shear flow and uniaxial elongation flow

Now we analyses the influence of parameters B and P (22) on the relation steady shear viscosity vs. shear rate. The calculations of steady and transient viscosimetric functions for the cases of simple shear and uniaxial elongation according to the model (19,22) follow those introduced in paragraph 3 for a one-mode case. Therefore, only the final results will be presented.

Figures 13 and 14 show that the curves describing a course of steady uniaxial elongational viscosity exhibit non-monotonous character with one or more inflexion points. The maximal value decreases with the increasing parameter B. The non-monotonous character converts to the monotonous one for $P = 0$. It shows that by the suitable choice of parameters B and
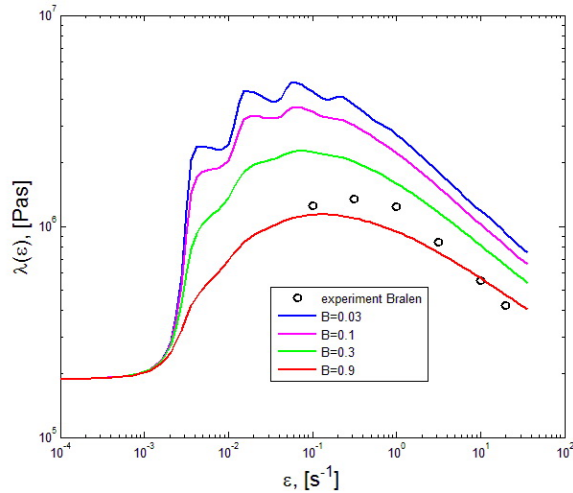
Figure 13: Relation of steady uniaxial elongation viscosity vs. elongation rate (constant $P = 0.001$) depending on parameter B.
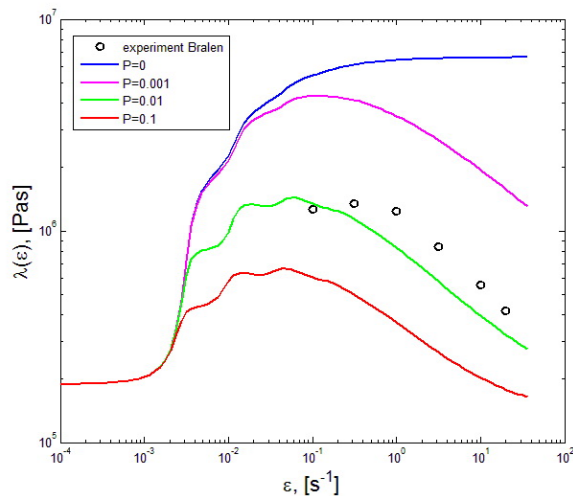

Figure 14: Relation of steady uniaxial elongation viscosity vs. elongation rate (constant $B = 0.2$) depending on parameter P.
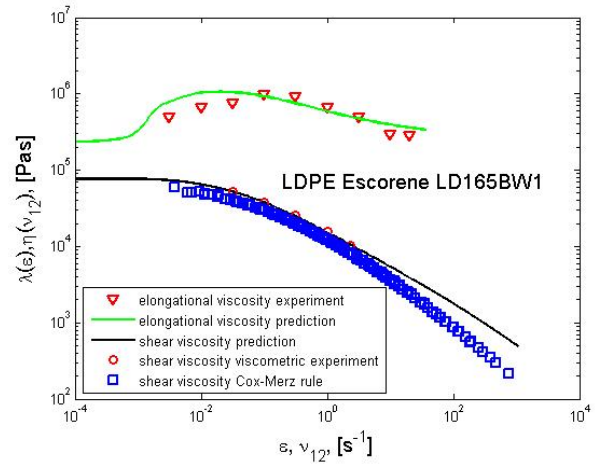

Figure 15: Comparison of the model predictions for for steady shear and elongational viscosity with the experimental data for Escorene [30].

P it is possible to describe a course of steady uniaxial elongational viscosity in dependence on elongation rate with sufficient accuracy. The question is whether with such determined B and P it is possible to describe steady and transient effects for simple shear and uniaxial elongation. Figures15,16 depicts the courses of steady shear and uniaxial elongation viscosity. It follows that the model (19) describes both viscosities with sufficient accuracy. It is obvious that Cox-Merz rule is fulfilled for the model [30].

Figures 17-20 show the courses of transient shear viscosity and the coefficient of the first normal stress difference in the case of simple shear. It follows that for low values of shear rates the passages to the limited stationary values are monotonous while for higher values the passages attain their maxima.

Figures 21,22 presents the courses of transient uniaxial elongation viscosity for various values of elongation rates. The calculation shows monotonous behaviour of elongation viscosity up to stabilized values. These values are attained more rapidly for higher values of extension rates. The model (19) depicts accurately the initial parts of viscosity curves. Similarly, the experimental data for higher extension rates is accompanied by non-smoothness. As this factor is not taken into account in the model (19), the prediction and experimental data for higher elongation rates differs. We should mention that this shortcoming is also present in other rheological models [33,34].

The calculations were carried out with the following choice of the parameters:$B = 0.5$, $P = 0.002$, $\alpha_0 = 6.5$ for Escorene and $B = 0.65$, $P = 0.002$, $\alpha_0 = 5$ for Bralen.

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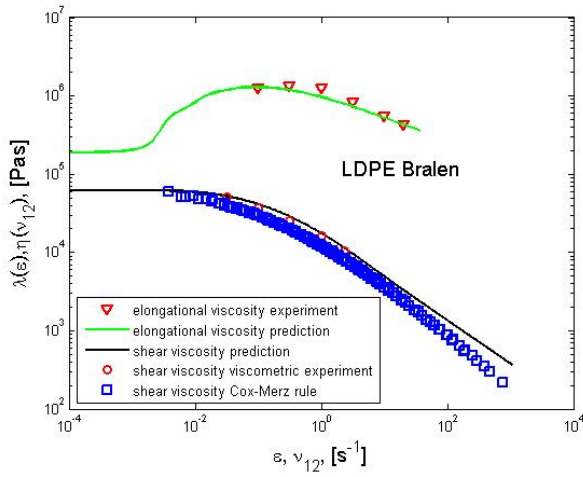Petr Filip, Radek Pivokonsky

Figure 16: Comparison of the model predictions for for steady shear and elongational viscosity with the experimental data for Bralen [30].
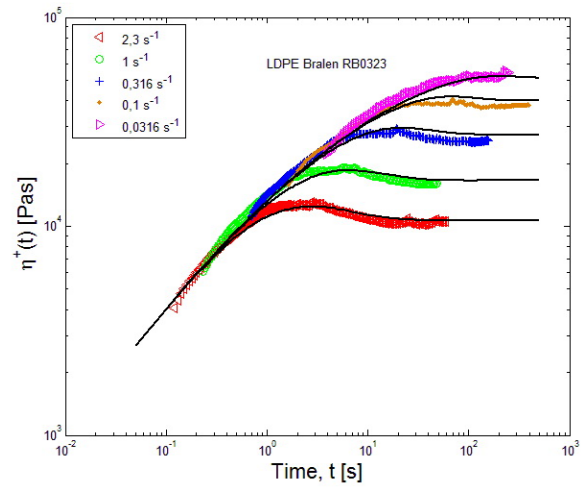

Figure 18: Comparison of the model predictions for transient shear viscosity with the experimental data for Bralen [30].
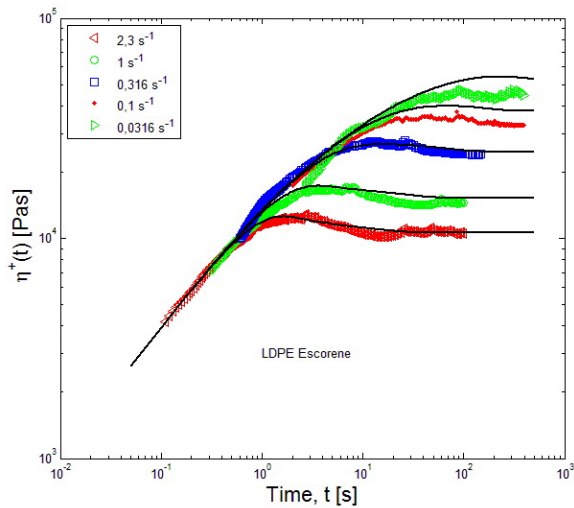

Figure 17: Comparison of the model predictions for transient shear viscosity with the experimental data for Escorene [30].
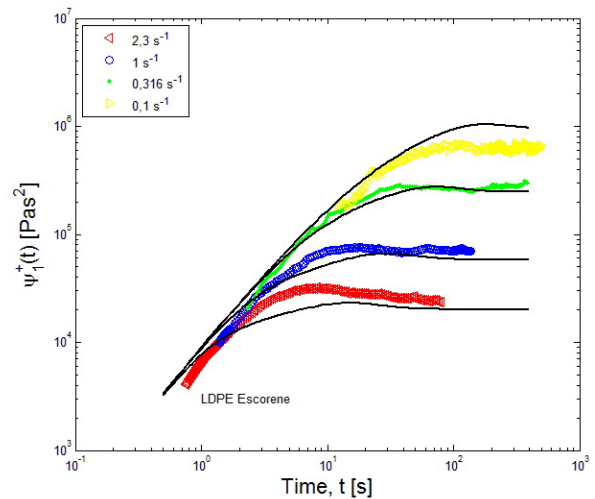

Figure 19: Comparison of the model predictions for the coefficient of the first normal stress difference with the experimental data for Escorene [30].
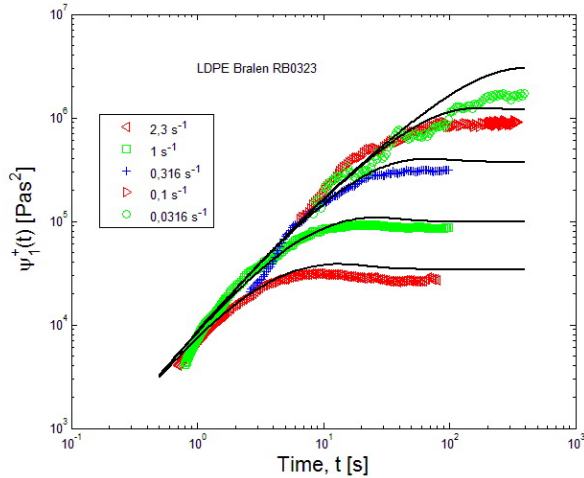
Figure 20: Comparison of the model predictions for the coefficient of the first normal stress difference with the experimental data for Bralen [30].
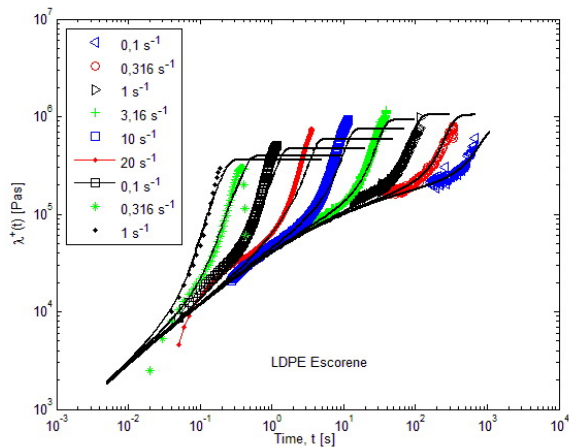

Figure 21: Comparison of the model predictions for transient uniaxial elongation viscosity with the experimental data for Escorene [30].
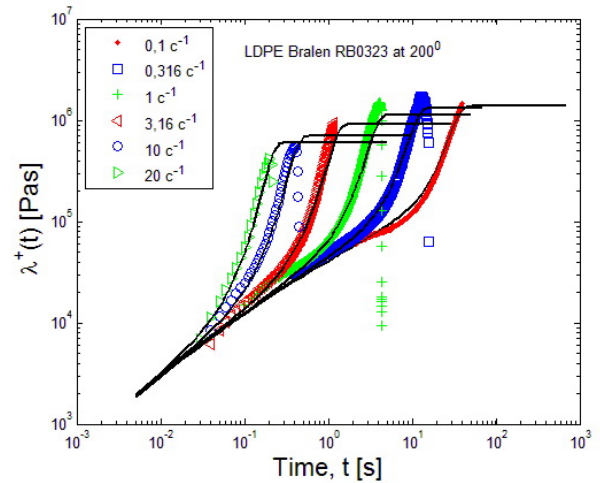

Figure 22: Comparison of the model predictions for transient uniaxial elongation viscosity with the experimental data for Bralen [30].

7 Conclusion

The papers [33,34] presents a comparison of the given experimental data with other rheological models such as Prokunin and Leonov model [2], the pom-pom model the extended Pom-Pom model[10-13]. The comparison of the experimental data with the predictions of other models shows that the introduced model (20) provides equivalent accuracy to the extended pom-pom model and better than the models in [2,10], and of course much better results when only one-mode approximation is used [24,27]. Based on the preceding comparisons, it is possible to conclude that the multi-mode model (19) describes steady and transient rheological characteristics of polymer melts with a sufficient accuracy. It is possible to expect that the model (19) is also applicable for high-concentrated polymer suspensions and linear polymer melts. This model is also possible to apply for more complex flows of polymer liquids, for example three-dimensional flow in the converning channel [31], or for investigate the stability of inhomogeneous flows [32].

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Table 1: Parameters g_α, τ_α and η_α for polymeric materials.

α	$g_\alpha, [Pa]$	$\tau_\alpha, [s]$	$\eta_\alpha, [Pa \cdot s]$	$g_\alpha, [Pa]$	$\tau_\alpha, [s]$	$\eta_\alpha, [Pa \cdot s]$
	LDPE Bralen RB0323			LDPE Escorene LD165BW1		
1	121440	0.00134	162.7	109430	0.00154	168,5
2	35290	0.0052	183.5	37350	0,00634	236,4
3	33443	0.0202	673.9	32409	0,026	843,3
4	19480	0.078	1520	15250	0,107	1630
5	11923	0.302	3604	11080	0,439	14710
6	5764	1.171	6749	4836	1,802	8704
7	2575	4.54	11680	1986,65	7,404	14710
8	800.9	17.57	14070	494,7	30,4	15046
9	213.4	68.07	14530	110,16	125	13760
10	34.69	263.7	9146	33,38	513	17126