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RHEOLOGICAL MODEL FOR DESCRIBING VISCOMETRIC FLOWS OF MELTS OF BRANCHED POLYMERS

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The present paper considers the problem of constructing a rheological constitutive relation for melts of branched polymers with the use of a modified Vinogradov–Pokrovskii rheological model generalized to the case of several noninteracting models, each of which corresponds to the account in the stress tensor of the contribution of a particular polymer fraction and is characterized by its own relaxation time and viscosity. Since the number of model parameters markedly increases thereby, simple dependences of its parameters on the mode number are proposed. On the basis of the obtained model, the nonlinear nonstationary effects at simple shear and uniaxial tensor have been considered.

Keywords: *rheology, polymer melts, mesoscopic approach, rheological equation of state, viscometric flows.*

Introduction. Experimental investigations of various polymer fluids point to their linear viscoelastic behavior. To investigate such effects, a large number of models describing the rheological behavior of polymer fluids at both qualitative and quantitative levels were proposed. It should be noted thereby that two radically different classes of models exist: models of the first class use the phenomenological approach, and in models of the second class the microscopic approach is used. In the phenomenological approach, the dynamics of macroscopic bodies is constructed on the basis of the general laws determined experimentally. This class of models includes the Maxwell, Oldroyd [1], and Prokunin–Leonov [2] phenomenological models. The other class of models is based on the mesoscopic approach. In such models, the macromolecular dynamics is described on the basis of model notions and, consequently, takes into account, in some approximation, both the structure of the polymer molecule and the processes of intermolecular interaction. Such models often use the one-molecule approximation in which instead of the whole aggregate of macromolecules, one chosen macromolecule moving in some "effective" medium is considered. In some of the models of this class the macromolecule is represented as a series of beads and springs (elastic force) connecting them. For example, one of the first of such models is the Kargin–Slonimskii–Rauz model. Thus, the mesoscopic approach, as opposed to the phenomenological one, makes it possible to follow the relationship between the micro- and macroscopic characteristics of polymer systems and, consequently, explain various phenomena in polymer melts, for example, the diffusion, viscoelasticity, and other phenomena. However, this approach requires the introduction of additional mesoscopic parameters, which should also be determined experimentally. Among the above models are also the Doi–Edwards [3], De Gennes [4], and Curtiss–Bird [5] models. In these models, each macromolecule is considered as a flexible chain moving inside some tube formed by other macromolecules; and at short observation times the molecule can move only along the tube. However, the initial Doi–Edwards model did not take into account the elongation of each segment of the polymer chain. It was later modified to take into account such elongation. The generalized model of "reptations" was described in [5], where the dynamics of the macromolecular chain was considered at two different levels — at the level of the macromolecule proper and at the level at which the tube model is discussed.

Another model [7] obtained from the theory of "reptations" was developed for describing the dynamics of branched polymers and is a rheological model in differential form. It is based on the dynamics of not beads connected in series, but of beads at the end of whose chain several beads are connected. This is the so-called "pom-pom" model. The disadvantage of the above model is the zero values of the second normal stress difference at simple shear. It was modified subsequently [8] and named the extended pom-pom model. These models consist of four differential equations containing an additional parameter that permits obtaining nonzero values of the second normal stress differences in shear flow.

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At present, different variants of the model of "reptations" are used most often to interpret experimental data in investigating the viscoelastic properties of solutions and melts. However, predictions of the theory do not always agree quantitatively with experiment, although their predictions are correct in general. In some works attempts were made to improve the quantitative agreement between the theory and experiments, which led to a theory of "dual reptations" where local entanglements are taken into account. The presence of long branches in the macromolecular chain leads to additional difficulties in using the "reptation" model, since in this case "reptations" become impossible, which requires modifying the model. Some works were specially devoted to the investigation of macromolecular chains with long lateral branches. For example, in [9], it was shown that the presence of long lateral branches in the macromolecule leads to the appearance of signs of the viscoelastic behavior, which is especially important in processes connected with the extension of polymer melts.

In the case of working with the Kargin–Slonimskii–Rauz model or the "beads–springs" model, the generalization is constructed by including in consideration the "internal viscosity," which permits describing the independence of the modulus value on the plateau of the molecular weight of the polymer. If only the slowest relaxation process in the polymer chain is considered thereby, one can go over to the Vinogradov–Pokrovskii model and, taking into account the induced anisotropy, to the modified Vinogradov–Pokrovskii model. This model, in spite of its simplicity, is adequate for viscoelastic flows of real polymer fluids. It describes such effects observed in practice as the first and the second normal stress difference, the increase in viscosity by tension, its going to a stationary value, and other phenomena. Moreover, a good agreement between theoretical and experimental dependences in a wide range of strain rates was noted.

The differential-vector RHL model [10] is also based on the microstructure approach. In this model, the macromolecular dynamics is described by one vector connecting the beginning and the end of the polymer chain. This vector can elongate with increasing length of the macromolecule, as well change its orientation under the action of the external flow. The RHL model is rather simple; however, its good agreement with experimental data was noted. This model actually made it possible to consider the orientation of the chain and its elongation separately with the nonlinear elasticity parameter of the coiled macromolecule, since it is based on the assumption that the orientation relaxation time is longer than the relaxation time of elongation.

At present, as before, much consideration is being given to the development of new models. For example, the authors of [11] made an attempt to solve the problem of describing the linear viscoelasticity of long-chain branched polymers. In spite of the large number of works devoted to the description of the dynamics of polymer media, of all the above-mentioned models, the most widely used ones are the Prokunin–Leonov model [2] and the "pom-pom" model [12] and its modifications [13]. Therefore, hereinafter we shall compare our results with the predictions of these models.

One more problem in the rheology of polymer fluids is the problem of taking into account the relaxation spectrum. The multimode character of the dynamics of polymer fluids or plurality of relaxation processes shows up already in the case of investigating flows of diluted solutions of flexible-chain monodisperse polymers [14–16]. This is mainly due to the chain character of the structure of polymer molecules. The dependences of the relaxation time on the model number obtained thereby are decaying, inversely proportional to the squared mode number or "Rauz-like" in nature. An increase in the polymer concentration in the system leads to the appearance of entanglements of macromolecules, their dynamics becomes more complex thereby, and between parts of the macromolecule "long-scale" interactions arise. This leads to additional terms in the stress tensor of the polymer system or to the account of new relaxation processes with "superslow" relaxation times [17–20]. The rheological relations obtained in the above works describe with good accuracy the relations of linear viscoelasticity, and the frequency dependences of the shear modulus and the loss modulus. Another important problem in the dynamics of polymer fluids is the description of nonlinear, gradient effects.

Apparently, in the case of describing the dynamics of a polydisperse sample or in the case where the macromolecule has a branched structure, plurality of relaxation processes plays an increasingly important role. The characteristics of the relaxation process (the relaxation time of the process and its weight in the stress tensor) no longer have the "Rauz-like" form and require generalization. In spite of this, it is necessary to use, as the basis for describing the dynamics of concentrated polymer systems, a fairly reliable rheological model obtained with the use of the mesoscopic approach. In this approach, model notions, for example, a "beads–springs" model, are used to describe the rather slow thermal motions of the macromolecule. Besides the Rauz parameters (drag coefficient of beads, equilibrium size of the coiled macromolecule), it is necessary to introduce into the model parameters taking into account the presence of entanglements in the polymer system. For such a model, we use in the present work the modified Vinogradov–Pokrovskii model [21–25]. The specific feature of this model is that it takes into account the tensor character of the drag coefficient of beads connected with the induced anisotropy of the shear flow. Such anisotropy is determined by the sizes and form of the coiled macromolecule and this leads to the appearance of corresponding coefficients in the dynamic equations. The generalization of this model to the multimode case was proposed in [26, 27] and has the form

$$\sigma_{ik} = -p\delta_{ik} + 3\sum_{\alpha=1}^{n} \frac{\eta_\alpha}{\tau_\alpha} a_{ik}^{\alpha} , \tag{1}$$

$$\frac{d}{dt} a_{ik}^{\alpha} - \nu_{ij} a_{jk}^{\alpha} - \nu_{kj} a_{ji}^{\alpha} + \frac{1 + (\kappa_\alpha - \beta_\alpha) a_{jj}^{\alpha}}{\tau_\alpha} a_{ik}^{\alpha} = \frac{2}{3}\gamma_{ik} - \frac{3\beta_\alpha}{\tau_\alpha} a_{ij}^{\alpha} a_{jk}^{\alpha} .$$

Here σ_{ik} is the stress tensor of the polymer system, ν_{ik} is the velocity gradient tensor, γ_{ik} is the symmetrized velocity gradient tensor, α is the ordinal mode number, n is the number of relaxation modes or processes taken into account, a_{ik}^{α} is the dimensionless tensor of additional stresses corresponding to the contribution with number α, a_{ij}^{α} is the trace of the tensor of additional stresses, η_α is the coefficient of shear viscosity of mode with number α, τ_α is the relaxation time of mode with number α, and $\kappa_\alpha = \kappa_\alpha(a_{ij}^{\alpha})$ and $\beta_\alpha = \beta_\alpha(a_{ij}^{\alpha})$ are parameters of the induced anisotropy determined by the expressions

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

In [17, 28], the constitutive equations were formulated initially in the multimode approximation and then simplified. In working with expressions (2), it was first assumed that the values of induced anisotropy parameters do not depend or depend weakly on the mode number; however, comparison with experiments showed that this assumption was incorrect; consequently, it was necessary to return to the multimode approximation. There is hope that the use of many relaxation modes for describing will lead to a better description of the available experimental results.

Since the influence of induced anisotropy parameters is different for each specific mode, it makes sense to consider each mode separately, which is reflected in writing expressions (2). To find κ_α, we used the relation $\kappa_\alpha = 1.2\beta_\alpha$ taken from [15].

Thus, the system of equations (1), (2) was determined with accuracy up to the parameters η_α, τ_α, f_α, and p_α that are to be determined from the experiment. The number of these parameters is rather large, especially at a large number of modes; therefore, it makes sense to consider the procedure of their determination in more detail.

Determination of Parameters of the Multimode Rheological Model. Obviously, the determining factor in choosing the rheological model is comparison with experimental data. Preference should be given thereby to such data that will be obtained for different samples and for which the values of some rheological characteristics will be close and the values of other characteristics will differ. Such a comparison made for two samples of branched polymers is given in [27, 29]. The constitutive relations were identified by the experimental data obtained in [27], where the rheology of two melts of the strongly branched low-density polyethylene used to obtain films (LDPE Bralen RB0323, Slovnaft, Slovakia and LDPE Escorene LD165BW1, Exxon, USA) was investigated. Experiments were performed at a temperature of 200°C. In [27], the elasticity modulus G' and the loss modulus G'' were measured by different methods, and the stresses, the transition and steady states of shear viscosity, and the coefficients of the first normal stress difference were determined. To obtain data at stationary shear and coefficients of the first normal stress difference at high rates of shear, an RH7 (Rosand Precision) capillary rheometer was used. The values of the first normal stress difference were obtained with the use of the method based on the determination of the outlet stress on the slit matrix. The viscosity at uniaxial tension was measured with the use of an ARES 2000 rheometer equipped with a universal SER-type testing platform (model SER-HV-A01, Xpansion Instruments). The experiment is described in detail in [29].

Let us first determine the parameters η_α and τ_α having viscosity and time dimensions, respectively. Solving the second equation of system (1) with accuracy up to first-order terms for velocity vectors, we obtain

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

This equation coincides with the Maxwell equation and we can obtain with its help the relations of linear viscoelasticity. From (1) and the last relation follow the formulas for calculating the elasticity and loss moduli, which can be obtained fairly easily [12]:

$$G'(\omega) = \sum_{\alpha=1}^{n} \frac{\omega^2 \tau_\alpha \eta_\alpha}{1 + (\omega\tau_\alpha)^2} , \quad G''(\omega) = \sum_{\alpha=1}^{n} \frac{\omega\eta_\alpha}{1 + (\omega\tau_\alpha)^2} . \tag{3}$$

TABLE 1. Values of the Linear Viscoelasticity Parameters

No.	g_α, Pa	τ_α, s	η_α, Pa·s	g_α, Pa	τ_α, s	η_α, Pa·s
	LDPE Bralen RB0323			LDPE Escorene LD165BW1		
1	121 440	0.00134	162.7	109 430	0.00154	168.5
2	35 292	0.0052	183.5	37 350	0.00633	236.4
3	33 443	0.0202	673.9	32 409	0.026	843.3
4	19 480	0.078	1520	15 250	0.107	1630
5	11 923	0.302	3604	11 080	0.439	14 710
6	5763.6	1.171	6749	4836	1.802	8704
7	2574.6	4.54	11 680	1986.65	7.404	14 710
8	800.9	17.57	14 070	494.7	30.4	15 046
9	213.4	68.07	14 530	110.16	125	13 760
10	34.69	263.7	9146	33.38	513	17 126

These relations agree with the results of calculations by other rheological models [28, 29], and the procedure of determining the parameters η_α and τ_α based on the minimization with the help of the least square technique is fairly reliable. The dynamic modulus components calculated by expressions (3) can be compared with experimental ones. Note that calculations were performed for ten modes, and the values of the model parameters chosen from the condition of the best agreement between experimental and calculated data are given in Table 1. The parameter η_α was determined by the formula $\eta_\alpha = g_\alpha \tau_\alpha$. This expression differs from the formula used in [26] by the coefficient 1/3 resulting from the setting up error. It should be noted that the values of g_α and τ_α were determined in [28]. Note that the combination of the parameters g_α and τ_α or η_α and τ_α is called the relaxation spectrum [28, 29].

To choose values of the anisotropy parameters, in [26] the contributions of each of the modes α were investigated, and the f_α and p_α values were determined on each portion of the stationary viscosity curve at uniaxial tension. It is clear that such a procedure cannot be called successful, since the model parameters were determined on the basis of intuitive relations. It was obtained thereby that both f_α and p_α are nonmonotonic functions of the mode number α. First these parameters increased with increasing α and then decreased, and their maxima fall at the middle of the range of change of the mode number: α = 5. Therefore, in the present paper we shall use for these parameters the expressions

$$f_\alpha = \frac{B}{1 + (\alpha - \alpha_0)^2}\,, \quad p_\alpha = \frac{P}{1 + (\alpha - \alpha_0)^2}\,. \tag{4}$$

In the latter relation, mode number α_0 corresponds to the numerical-mean value of the molecular mass M_n. It might be expected that the form and sizes of the coiled macromolecule corresponding to M_n will have the strongest effect on the polymer fluid dynamics. Those fractions whose molecular mass differs considerably from M_n should have an insignificant influence on the nonlinear viscoelastic properties of such a medium. This means that at $\alpha \to \infty$ the parameters f_α and p_α will be infinitely small. Naturally, in reality this limiting transition is unrealizable; nevertheless, for a mode number difference equal to 5, their influence weakens 25 times.

Viscoelastic Functions at Simple Shear and Uniaxial Tension. Let us consider the influence of the parameters B and P introduced into expression (4) on the form of the dependence of the stationary shear viscosity on the rate of shear. Numerical calculations of nonstationary viscometric functions at simple shear and uniaxial tension by model (1), (2), (4) were carried out by the Runge–Kutta method, and their stationary values were obtained by the settling method. Details of the calculations performed for the single-mode model are given in [20]. Therefore, we present only the final results.

From Fig. 1 it is seen that the curve of the stationary viscosity as a function of the extension rate is nonmonotonic and has one or several inflection points. As the parameter B increases, the maximum value on this curve decreases. At $P = 0$ the nonmonotonic character of the curve changes for the monotonic character. Thus, it is seen that selecting the parameters B and P permits describing fairly accurately the dependence of the stationary viscosity on the extension rate. Now let us see

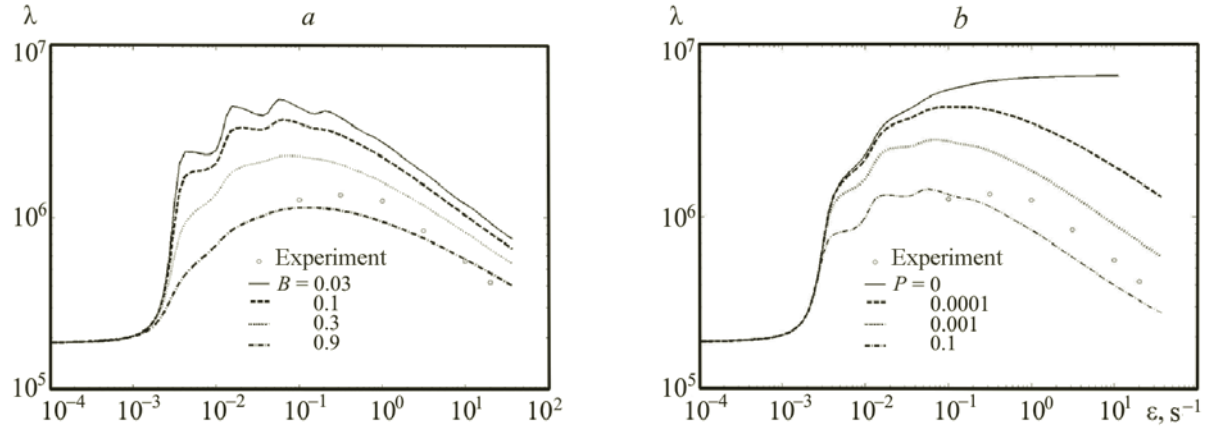

Fig. 1. Influence of the parameters B (a) and P (b) on the dependence of the stationary viscosity of the melt on its extension rates: a) $P = 0.001$; b) $B = 0.2$.

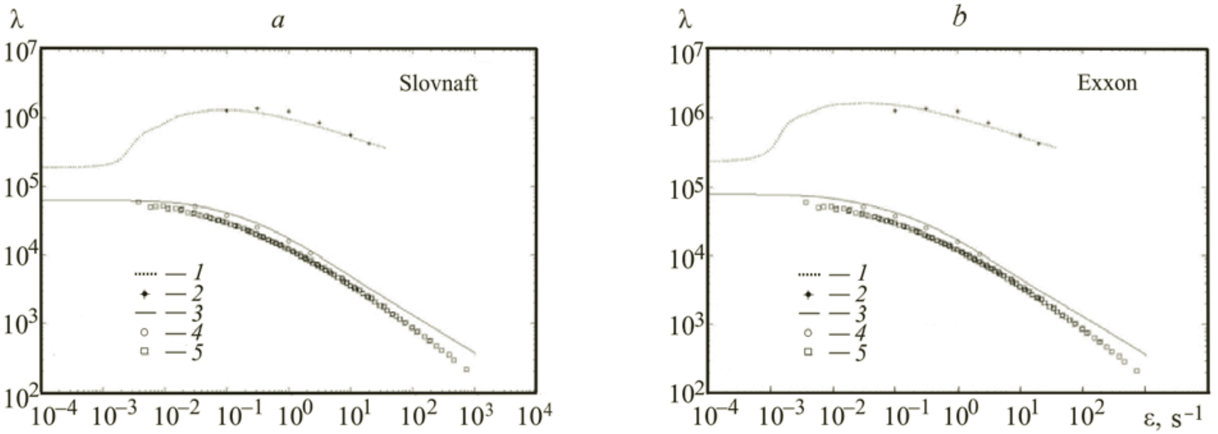

Fig. 2. Comparison of the gradient dependences of stationary viscosities of the Slovnaft (a) and Exxon (b) melts at tension (1, 2) and simple shear (3, 4) at a temperature of 200°C: 1, 3) calculation; 2, 4) experiment [28]; 5) oscillation experiment (Cox–Merz rule).

if we can describe, with the help of the parameters B and P found for the stationary viscosity extension, the nonstationary effects at simple shear and uniaxial tension. Figure 2 shows the gradient dependences of viscosity at shear and tension. From this figure it is seen that model (2) describes with fair accuracy the shear viscosity anomaly and the nonuniform dependence of the elongation viscosity and that for this model the Cox–Merz rule holds [10].

Figure 3 shows the time dependences of viscosity setting, the coefficient of the first normal stress difference at simple shear, and the viscosity at uniaxial tension of the Slovnaft and Exxon melts, as well as the nonstationary dependences of viscosity settling at uniaxial tension. From Fig. 3a, b, c, and d it is seen that at low rates of shear the measured values go monotonically to the steady state, and at high rates of shear the measured dependences go through the maximum. It should be noted that model (1) describes fairly well the initial portion of the considered dependences. At the same time, in experiments, destruction of samples at high extension rates is observed. Since this phenomenon was not taken into account in model (1), at large times the behavior of the model and of the experimental sample differs considerably. This disadvantage is also present in other rheological models [28, 29]. Note that all calculations were performed at certain values of parameters different for different samples. In particular, for Escorene they had values of $B = 0.5$, $P = 0.002$, and $\alpha_0 = 6.5$, and for Bralen $B = 0.65$, $P = 0.002$, and $\alpha_0 = 5$. Thus, instead of the intuitive procedure of determining the parameters of the rheological model used in [26], here a more reliable procedure based on expressions (4) is proposed. It should also be noted that in [29] comparison was made between the obtained experimental data and calculations performed by other rheological models: the modified Prokunin–Leonov model [2], the pom-pom model [12], and the expanded pom-pom model [13].

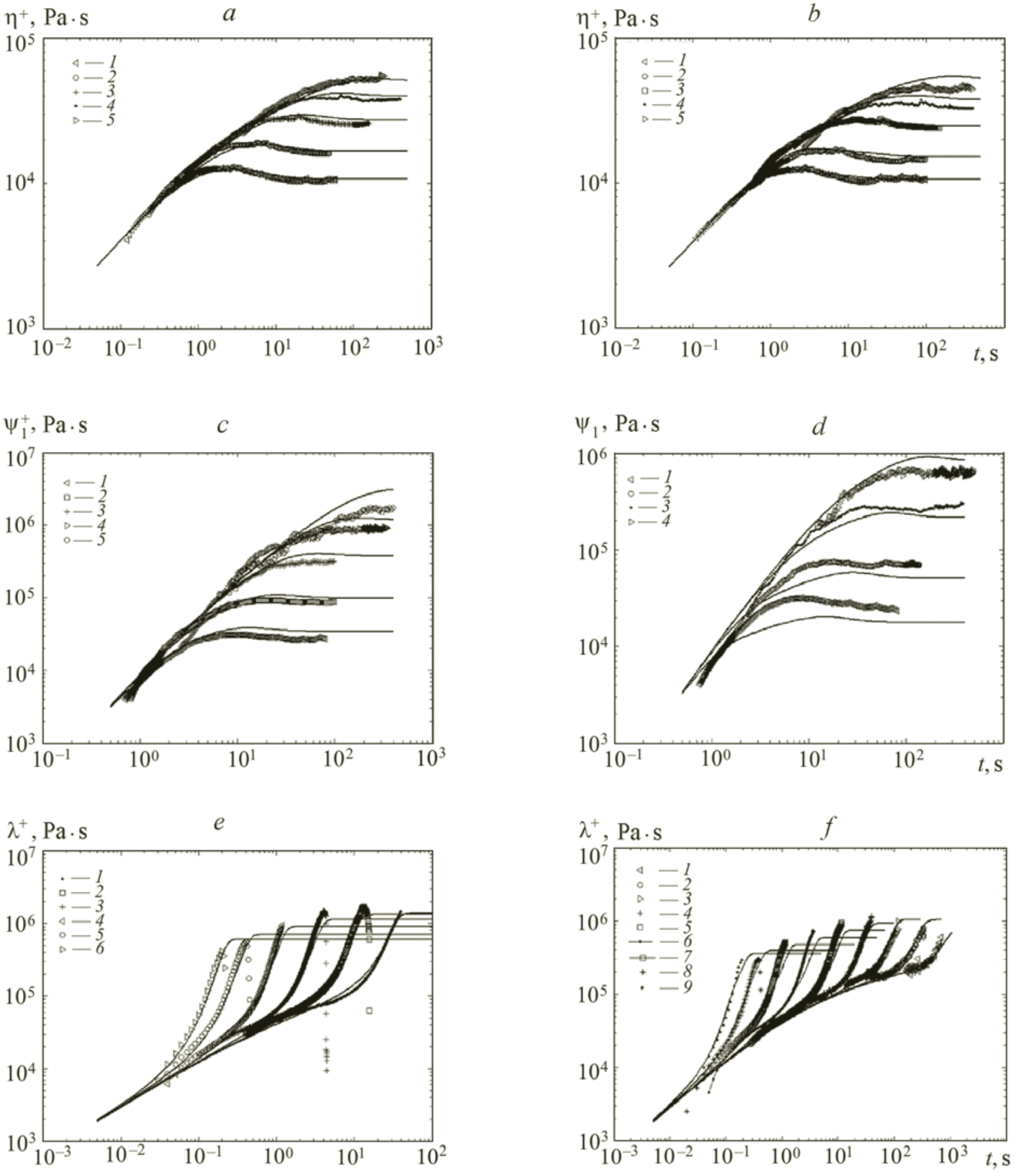

Fig. 3. Comparison of the time dependences of settling of the shear viscosity (a, b), the coefficient of the first normal stress difference (c, d), and viscosity at uniaxial tension (e, f) of the Slovnaft (a, c, e) and Exxon (b, d, e) melts at various rates of shear (a, b, c, d), and extension rates (e, f): a–d) 1) $\varepsilon = 2.3$ s^{-1}; 2) 1; 3) 0.316; 4) 0.1; 5) 0.0316; e, f) 1) $\varepsilon = 0.1$ s^{-1}; 2) 0.316; 3) 1; 4) 3.16; 5) 10; 6) 20; 7) 0.1; 8) 0.316; 9) 1.

The results of the comparison of the experimental data with the calculations by other models show that model (1) provides an accuracy of predictions not worse than the expanded pom-pom model and better results than the models of [2] and [12], as well as much better results as compared to the one-mode approximation [21, 26].

Conclusions. A comparison between the results of calculations and the corresponding experimental data has shown that although the proposed multimode model was obtained as a development of theoretical notions about the dynamics of linear polymer chains, it permits describing with fair accuracy the stationary and nonstationary dependences of the viscometric functions of melts of branched polymers on the velocity gradients. It might be expected thereby that the obtained model will turn out to be also suitable for concentrated solutions and melts of linear polymers. This model can also be used to describe more complex flows of polymer fluid media

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NOTATION

G' and G'', elasticity and loss moduli; M_n, mean numerical value of the molecular mass; p, hydrostatic pressure; t, time, s; ε, extension rate or rate of shear; η, shear-viscosity coefficient; λ, viscosity coefficient at uniaxial tension; ω, oscillation frequency.

REFERENCES

1. J. G. Oldroyd, On the formulation of rheological equations of state, *Proc. R. Soc. London*, **A200**, 523–541 (1950).
2. A. I. Leonov and A. N. Prokunin, *Nonlinear Phenomena in Flows of Viscoelastic Polymer Fluids*, Chapman and Hall, New York (1994).
3. M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford, Clarendon (1986).
4. De Gennes, *PG Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca (1979).
5. R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Fluids*, Vol. 2, Wiley, New York, (1987).
6. H. C. Ottinger, A thermodynamically admissible reptation model for fast flows of entangled polymer, *J. Rheol*., **43**, 1461–1493 (1999).
7. T. C. B. McLeish and R. G. Larson, Molecular constitutive equations for a class of branched polymers: the pom-pom polymer, *J. Rheol.*, **42**, 81–110 (1998).
8. W. M. H. Verbeeten, G. W. M. Peters, and F. P. T. Baaijens, Differential constitutive equations for polymer melt: the extended pom-pom model, *J. Rheol*., **45**, 821–841 (2001).
9. M. Zatloukal, Differential viscoelastic constitutive equations for polymer melts in steady shear and elongational flow, *J. Non-Newtonian Fluid Mech*., **209**, 11–27 (2003).
10. J. Remmelgas, G. Harrison, and L. G. Leal, A differential constitutive equation for entangled polymer solutions, *J. Non-Newton Fluid*, **80**, Nos. 2–3, 115–134 (1999).
11. T. Borg and E. J. Pääkkönen, Linear viscoelastic model for elongational viscosity by control theory, *Rheol. Acta*, **13**, 371–384 (2011).
12. G. Bishko, T. C. B. McLeish, O. G. Harlen, and R. G. Larson, Theoretical molecular rheology of branched polymers in simple and complex flows: the pom-pom model, *Phys. Rev. Lett*., **79**, No. 12, 2352–2355 (1997).
13. W. M. H. Verbeeten, G. W. M. Peters, and F. P. T. Baaijens, Differential constitutive equations for polymer melts: the extended pom-pom model, *J. Rheol*., **45**, 823–843 (2001).
14. V. A. Kargin and G. A. Slonimskii, On the deformation of amorphous-liquid linear polymers, *Dokl. Akad. Nauk SSSR*, **62**, No. 2, 239–242 (1948).
15. P. E. A. Rouse, Theory of the linear viscoelastic properties of dilute solutions of cooling polymers, *J. Chem. Phys*., **21**, No. 7, 1271–1280 (1953).
16. W. W. Graessley, The entanglement concept in polymer rheology, *Adv. Polym. Sci*., **16**, 1–179 (1974).
17. V. N. Pokrovskii and G. V. Pyshnograi, Simple forms of the constitutive equation of concentrated solutions and melts of polymers as a corollary of the molecular theory of viscoelasticity, *Izv. Akad. Nauk SSSR*, *Mekh Zhidk. Gaza*, No. 1, 71–77 (1991).
18. V. N. Pokrovskii and V. S. Volkov, Computation of the relaxation times and dynamic modulus of linear polymers on the basis of the monomolecular approximation with self-consistency (a new approach to the theory of viscoelasticity of linear polymers), *Vysokomol. Soedin*., A**20**, No. 12, 2700–2706 (1978).

19. V. N. Pokrovskii, Dynamics of loosely bound linear macromolecules, *Usp. Fiz. Nauk*, **162**, No. 5, 87–121 (1992).
20. Yu. A. Altukhov, A. S. Gusev, G. V. Pyshnograi, and K. B. Koshelev, *Introduction to the Mesoscopic Theory of Fluid Polymer Systems* [in Russian], Izd. AltGPA, Barnaul (2012).
21. G. V. Pyshnograi, V. N. Pokrovskii, Yu. G. Yanovskii, Yu. N. Karnet, and I. F. Obraztsov, Constitutive equation of nonlinear viscoelastic (polymer) media in the zeroth approximation for parameters of the molecular theory and corollary for shear and tension, *Dokl. Akad. Nauk*, **339**, No. 5, 612–615 (1994).
22. G. V. Pyshnograi, A. S. Gusev, and V. N. Pokrovskii, Constitutive equations for weakly entangled linear polymers, *J. Non-Newtonian Fluid Mech*., **163**, Nos.1–3, 17–28 (2009).
23. I. É. Golovicheva, S. A. Zinovich, and G. V. Pyshnograi, Influence of molecular mass on the shear and longitudinal viscosity of linear polymers, *Prikl. Mekh. Tekh. Fiz*., **41**, No. 2, 154–160 (2000).
24. A. S. Gusev, M. A. Makarova, and G. V. Pyshnograi, Mesoscopic equation of state of polymer media and description of the dynamic characteristics based on it, *J. Eng. Phys. Thermophys*., **78**, No. 5, 892–898 (2005).
25. Al Joda H. N. A., G. L. Afonin, D. A. Merzlikina, P. Filip, R. Pivokonskii, and G. V. Pyshnograi, Modification of the law of internal friction in the mesoscopic theory of fluid polymer media, *Mekh. Kompozit. Mater. Konstr.*, **19**, No. 1, 128–140 (2013).
26. D. A. Merzlikina, P. Filip, R. Pivokonskii, and G. V. Pyshnograi, Multimode rheological model and corollaries for simple shear and tension, *Mekh. Kompozit. Mater. Konstr.*, **19**, No. 2, 254–261 (2013).
27. V. N. Pokrovskii, *The Mesoscopic Theory of Polymer Dynamics*, 2nd edn., Springer, Dordrecht–Heidelberg–London–New York (2010).
28. V. H. Rolón-Garrido, R. Pivokonsky, P. Filip, M. Zatloukal, and M. H. Wagner, Modelling elongational and shear rheology of two LDPE melts, *Rheol. Acta*, **48**, 691–697 (2009).
29. R. Pivokonsky, M. Zatloukal, and P. Filip, On the predictive/fitting capabilities of the advanced differential constitutive equations for branched LDPE melts, *J. Non-Newtonian Fluid Mech*., **135**, 58–67 (2006).