

Introduction The viscosity  $\eta$  of polymeric solutions is an object of the numerous experimental and theoretical investigations generalized in ref. [1-4]. This is explained both by the practical importance of the presented property of polymeric solutions in a number of the technological processes and by the variety of the factors having an influence on the  $\eta$  value, also by a wide diapason (from  $10^{-3}$  to  $10^2$  Pa·s) of the viscosity change under transition from the diluted solutions and melts to the concentrated ones. The all above said gives a great informational groundwork for the testing of different theoretical imaginations about the equilibrium and dynamic properties of the polymeric chains. It can be marked three main peculiarities for the characteristic of the concentrated polymeric solutions viscosity, namely: 1. Measurable effective viscosity  $\eta$  for the concentrated solutions is considerable stronger than the  $\eta$  for the diluted solutions and depends on the velocity gradient  $g$  of the hydrodynamic flow or on the shear rate. It can be distinguished [4] the initial  $\eta_0$  and the final  $\eta_\infty$  viscosities ( $\eta_0 > \eta_\infty$ ), to which the extreme conditions  $g \rightarrow 0$  and  $g \rightarrow \infty$  correspond respectively. Due to dependence of  $\eta$  on  $g$  and also due to the absence of its theoretical description, the main attention of the researches [4] is paid into, so-called, the most newton (initial) viscosity  $\eta_0$ , which is formally determined as the limited value at  $g \rightarrow 0$ . Exactly this value  $\eta_0$  is estimated as a function of molar mass, temperature, concentration (in solutions). The necessity of the experimentally found values of effective viscosity extrapolation to «zero» shear stress doesn't permit to obtain the reliable value of  $\eta_0$ . This leads to the essential and far as always easy explained contradictions of the experimental results under the critical comparison of data by different authors. 2. Strong power dependence of  $\eta$  on the length  $N$  of a polymeric chain and on the concentration  $r$  (g/m<sup>3</sup>) of a polymer in solution exists: with the indexes  $\alpha = 5, 7$ ,  $b = 3,3, 3,5$ , as it was shown by authors [4]. 3. It was experimentally determined by authors [1, 5] that the viscosity  $\eta$  and the characteristic relaxation time  $t^*$  of the polymeric chains into concentrated solutions and melts are characterized by the same scaling dependence on the length of a chain: (1) with the index  $b = 3,4$ . Among the numerous theoretical approaches to the analysis of the polymeric solutions viscosity anomaly, i. e. the dependence of  $\eta$  on  $g$ , it can be marked the three main approaches. The first one connects the anomaly of the viscosity with the influence of the shear strain on the potential energy of the molecular kinetic units transition from the one equilibrium state into another one and gives the analysis of this transition from the point of view of the absolute reactions rates theory [6]. However, such approach hasn't take into account the specificity of the polymeric chains; that is why, it wasn't win recognized in the viscosity theory of the polymeric solutions. In accordance with the second approach the polymeric solutions viscosity anomaly is explained by the effect of the hydrodynamic interaction between the links of the polymeric chain; such links represent by themselves the «beads» into the «necklace» model. Accordingly to this effect the hydrodynamic flow around the presented "bead" essentially depends on the position of the other «beads» into the

polymeric ball. An anomaly of the viscosity was conditioned by the anisotropy of the hydrodynamic interaction which creates the orientational effect [7, 8]. High values of the viscosity for the concentrated solutions and its strong gradient dependence cannot be explained only by the effect of the hydrodynamic interaction. That is why the approaches integrated into the conception of the structural theory of the viscosity were generally recognized. In accordance with this theory the viscosity of the concentrated polymeric solutions is determined by the quasi-net of the linkages of twisted between themselves polymeric chains and, therefore, depends on the modulus of elasticity  $E$  of the quasi-net and on the characteristic relaxation time  $t^*$  [1-2]: (2) It is supposed, that the  $E$  is directly proportional to the density of the linkages assemblies and is inversely proportional to the interval between them along the same chain. An anomaly of the viscosity is explained by the linkages assemblies' density decreasing at their destruction under the action of shear strain [9], or by the change of the relaxation spectrum [10], or by the distortion of the polymer chain links distribution function relatively to its center of gravity [11]. A gradient dependence of the viscosity is described by the expression [11]: (3) It was greatly recognized the universal scaling ratio [1, 5]: (4) in which the dimensionless function has the asymptotes  $f(0) = 1$ ,  $f(x)x \gg 1 = x^{-g}$ ,  $g = 0,8$ . Hence, both expressions (3) and (4) declare the gradient dependence of  $\eta$  by the function of the one non-dimensional parameter  $gt^*$ . However, under the theoretical estimation of  $\eta$  and  $t^*$  as a function of  $N$  there are contradictions between the experimentally determined ratio (1) and  $b = 3,4$ . Thus, the analysis of the entrainment of the surrounding chains under the movement of some separated chain by [12] leads to the dependencies but . At the analysis [13] of the self-coordinated movement of a chain enclosing into the tube formed by the neighbouring chains it was obtained the , . The approach in [14] which is based on the conception of the reptational mechanism of the polymeric chain movement gives the following dependence . So, the index  $b = 3,4$  in the ratio (1) from the point of view of authors [2] remains by one among the main unsolved tasks of the polymers' physics. Summarizing the above presented short review, let us note, that the conception about the viscosity-elastic properties of the polymeric solutions accordingly to the Maxwell's equation should be signified the presence of two components of the effective viscosity, namely: the frictional one, caused by the friction forces only, and the elastic one, caused by the shear strain of the conformational volume of macromolecules. But in any among listed above theoretical approaches the shear strain of the conformational volumes of macromolecules was not taken into account. The sustained opinion by authors [3-4] that the shear strain is visualized only in the strong hydrodynamic flows whereas it can be neglected at little  $g$ , facilitates to this fact. But in this case the inverse effect should be observed, namely an increase of  $\eta$  at the  $g$  enlargement. These contradictions can be overpassed, if to take into account [15, 16], that, although at the velocity gradient of hydrodynamic flow increasing the external action leading to the shear strain of the conformational volume of polymeric chain is increased, but at

the same time, the characteristic time of the external action on the rotating polymeric ball is decreased; in accordance with the kinetic reasons this leads to the decreasing but not to the increasing of the shear strain degree. Such analysis done by authors [15-17] permitted to mark the frictional and the elastic components of the viscosity and to show that exactly the elastic component of the viscosity is the gradiently dependent value. The elastic properties of the conformational volume of polymeric chains, in particular shear modulus, were described early by authors [18-19] based on the self-avoiding walks statistics (SAWS). Here presented the experimental data concerning to the viscosity of the concentrated solutions of styrene in toluene and also of the melt and it is given their interpretation on the basis of works [15-19].

Experimental data and starting positions In order to obtain statistically significant experimental data we have studied the gradient dependence of the viscosity for the concentrated solution of polystyrene in toluene at concentrations  $0,4 \times 10^5$ ;  $0,5 \times 10^5$  and  $0,7 \times 10^5$  g/m<sup>3</sup> for the four fractions of polystyrene characterizing by the apparent molar weights  $M = 5,1 \times 10^4$ ;  $M = 4,1 \times 10^4$ ;  $M = 3,3 \times 10^4$  and  $M = 2,2 \times 10^4$  g/mole. For each pair of values  $r$  and  $M$  the gradient dependence of the viscosity has been studied at fourth temperatures 25 0C, 30 0C, 35 0C and 40 0C. The experiments have been carried out with the use of the rotary viscometer RHEOTEST 2.1 equipped by the working cylinder having two rotary surfaces by diameters  $d_1 = 3,4 \times 10^{-2}$  and  $d_2 = 3,9 \times 10^{-2}$  m. Results and discussion: concentrated solutions Initial statements Typical dependences of viscosity  $\eta$  of solution on the angular velocity  $\omega$  (turns/s) of the working cylinder rotation are represented on Fig. 1-3. Generally it was obtained the 48 curves of  $h(\omega)$ . For the analysis of the experimental curves of  $h(\omega)$  it was used the expression [15, 20]: (5) in which  $\eta$  is the measured viscosity of the solution at given value  $\omega$  of the working cylinder velocity rate;  $\eta_f$ , and  $\eta_e$  are frictional and elastic components of  $\eta$ ; (6) where is the characteristic time of the shear strain of the conformational volume for m-ball of intertwined polymeric chains; is the characteristic time of the external action of gradient rate of the hydrodynamic flow on the m-ball. The notion about the m-ball of the intertwined polymeric chains will be considered later. The shear strain of the conformational volume of m-ball and its rotation is realized in accordance with the reptational mechanism presented in ref. [2], i. e. via the segmental movement of the polymeric chain, that is why is also the characteristic time of the own, i. e. without the action  $g$ , rotation of m-ball [17]. Fig. 1 – Experimental (points) and calculated in accordance with the equation (5) (curves) dependencies of the effective viscosity on the rotation velocity of the working cylinder:  $\rho = 4,0 \cdot 10^5$  g/m<sup>3</sup>,  $M = 4,1 \cdot 10^4$  g/mole,  $T = 25 \div 40$  0C The expression (5) leads to the two asymptotes: at at  $S_0$ , it is observed a general regularity of the effective viscosity dependence on the rotation velocity  $\omega$  of the working cylinder for diluted, concentrated solutions and melts. Under condition, that , that is at , the effective viscosity is equal to a sum of the frictional and elastic components of the viscosity, and under condition the measurable viscosity is determined only by a frictional component

of the viscosity. In accordance with eq. (5) the effective viscosity  $\eta(\omega)$  is a function on three parameters, namely  $\eta_f$ ,  $\eta_e$  and  $b$ . They can be found on a basis of the experimental values of  $\eta(\omega)$  via the optimization method in program ORIGIN 5.0. As an analysis showed, the numerical values of  $\eta_f$  and  $\eta_e$  are easily determined upon a plateau on the curves  $\eta(\omega)$  accordingly to the condition (see Figures 1-3). However, the optimization method gave not always the correct values of  $\eta_f$  and  $\eta_e$ . There are two reasons for this. Firstly, in a field of the uncertainty of  $\eta(\omega)$  measurement is sharply increased since the moment of force registered by a device is a small. Secondly, in very important field of the curve transition  $\eta(\omega)$  from the strong dependence of  $\eta$  on  $\omega$  to the weak one the parameters  $\eta_f$  and  $b$  are interflowed into a composition  $b$ , i. e. they are by one parameter. Really, at the condition decomposing the exponents into (5) and limiting by two terms of the row  $\eta_e \omega^2$ , we will obtain  $\eta(\omega) = \eta_f + b \omega^2$ . Due to the above-mentioned reasons the optimization method gives the values of  $\eta_f$  and  $b$  depending between themselves but doesn't giving the global minimum of the errors functional. That is why at the estimation of  $\eta_f$  and  $b$  parameters it was necessary sometimes to supplement the optimization method with the «manual» method of the global minimum search varying mainly by the numerical estimation of  $b$ . Fig. 2 - Experimental (points) and calculated in accordance with the equation (5) (curves) dependencies of the effective viscosity on the rotation velocity of the working cylinder:  $\rho = 5.0 \cdot 10^5 \text{ g/m}^3$ ,  $M = 5.1 \div 2.2 \cdot 10^4 \text{ g/mole}$ ,  $T = 25 \text{ }^\circ\text{C}$  Fig. 3 - Experimental (points) and calculated in accordance with the equation (5) (curves) dependencies of the effective viscosity on the rotation velocity of the working cylinder:  $\rho = 4.0 \cdot 10^5 \text{ , } 7.0 \cdot 10^5 \text{ g/m}^3$ ,  $M = 3.3 \cdot 10^4 \text{ g/mole}$ ,  $T = 25 \text{ }^\circ\text{C}$  As we can see from the Figures 1-3, calculated curves  $\eta(\omega)$  accordingly to the equation (5) and found in such a way parameters  $\eta_f$ ,  $\eta_e$  and  $b$ , are described the experimental values very well. The results of  $\eta_f$ ,  $\eta_e$  and  $b$  numerical estimations for the all 48 experimental curves  $\eta(\omega)$  are represented in Table 1. The mean-square standard deviations of the  $\eta_f$ ,  $\eta_e$  and  $b$  calculations indicated on the Figures. A review of these data shows that the all three parameters are the functions on the concentration of polymer into solution, on the length of a chain and on the temperature. But at this, the  $\eta_f$  and  $\eta_e$  are increased at the  $\rho$  and  $M$  increasing and are decreased at the  $T$  increasing whereas the  $b$  parameter is changed into the opposite way. The analysis of these dependencies will be represented further. Here let us present the all needed for this analysis determinations, notifications and information concerning to the concentrated polymeric solutions. Investigated solutions of the polystyrene in toluene were concentrated; since the following condition was performing for them:  $\rho > \rho_c$ , (7) where  $\rho_c$  is a critical density of the solution per polymer corresponding to the starting of the polymeric chains conformational volumes overlapping having into diluted solution the conformation of Flory ball by the radius  $r$ , (8) here  $a$  is a length of the chain's link. It's followed from the determination of  $r$ , (9) where  $M_0$  is the molar weigh of the link of a chain. Taking into account the eq. eq. (8) and (9) we have:  $r = a \sqrt{M/M_0}$ , (10) where (11) can be called as the density into volume of the monomeric link. In accordance with the

SARWS [19] the conformational radius  $R_m$  of the polymeric chain into concentrated solutions is greater than into diluted ones and is increased at the polymer concentration increasing. Moreover, not one, but  $m$  macromolecules with the same conformational radius are present into the conformational volume. This leads to the notion of twisted polymeric chains  $m$ -ball for which the conformational volume is general and equally accessible. Since the  $m$ -ball is not localized with the concrete polymeric chain, it is the virtual, i. e. by the mathematical notion. It is followed from the SARWS [19]: (12) at, (13) thus, it can be written (14) Table 1 - Optimization parameters  $\eta_f$ ,  $\eta_e$  and  $b$  in equation (5)  $\rho \cdot 10^{-5}$ , g/m<sup>3</sup> 4,0 5,0 7,0 T, °C  $M \cdot 10^4$  g/mole 5,1 4,1 3,3 2,2 5,1 4,1 3,3 2,2 5,1 4,1 3,3 2,2 25  $\eta_f \cdot$ , Pa·s 0,35 0,19 0,16 0,06 1,11 0,69 0,43 0,36 6,50 2,66 2,64 0,86  $\eta_e$ , Pa·s 1,40 0,73 0,33 0,09 2,50 1,10 0,87 0,35 7,60 3,75 2,37 1,50  $b \cdot 10^3$ , s<sup>-1</sup> 1,15 3,37 4,20 32,3 1,66 1,02 2,91 7,31 0,36 0,76 1,50 2,44 30  $\eta_f \cdot$ , Pa·s 0,31 0,17 0,14 0,05 1,00 0,62 0,36 0,24 4,95 2,11 2,03 0,68  $\eta_e$ , Pa·s 0,95 0,57 0,25 0,06 1,30 0,76 0,52 0,32 4,05 2,21 1,86 1,00  $b \cdot 10^3$ , s<sup>-1</sup> 1,38 4,30 5,90 35,0 2,23 1,80 3,14 8,69 0,72 0,83 1,70 2,65 35  $\eta_f \cdot$ , Pa·s 0,19 0,13 0,11 0,04 0,68 0,50 0,26 0,19 4,07 1,85 1,45 0,43  $\eta_e$ , Pa·s 0,60 0,39 0,21 0,05 0,90 0,35 0,23 0,22 3,50 1,80 1,59 0,79  $b \cdot 10^3$ , s<sup>-1</sup> 3,67 5,80 6,37 49,0 2,41 3,56 4,60 9,10 0,88 0,96 1,93 3,20 40  $\eta_f \cdot$ , Pa·s 0,17 0,12 0,10 0,04 0,56 0,42 0,22 0,17 2,91 1,46 0,98 0,27  $\eta_e$ , Pa·s 0,40 0,19 0,13 0,03 0,65 0,29 0,15 0,12 2,01 1,39 1,19 0,57  $b \cdot 10^3$ , s<sup>-1</sup> 5,35 6,60 6,90 73,9 2,67 5,60 5,60 16,8 1,33 1,41 2,27 4,24

The shear modulus for the  $m$ -ball was determined by the expression [19]: (15) and, as it can be seen, doesn't depend on the length of a chain into the concentrated solutions. Characteristic time of the rotary movement of the  $m$ -ball and, respectively its shear, in accordance with the prior work [17] is equal to (16) Let us compare the with the characteristic time of the rotary movement of Flory ball into diluted solution [17]: . (17) In these expressions and are characteristic times of the segmental movement of the polymeric chains and and are their form factors into concentrated and diluted solutions respectively. Let us note also, that the expressions (16) and (17) are self-coordinated since at the expression (16) transforms into the eq. (17). The form factors and are determined by a fact how much strong the conformational volume of the polymeric chain is strained into the ellipsoid of rotation, flattened or elongated one as it was shown by author [21].

Frictional component of the effective viscosity In accordance with the data of Table 1 the frictional component of the viscosity strongly depends on a length of the polymeric chains, on their concentration and on the temperature. The all spectrum of dependence on  $N$ , and  $T$  we will be considered as the superposition of the fourth movement forms giving the endowment into the frictional component of the solution viscosity. For the solvent such movement form is the Brownian movement of the molecules, i. e. their translation freedom degree: the solvent viscosity coefficient will be corresponding to this translation freedom degree. The analogue of the Brownian movement of the solvent molecules is the segmental movement of the polymeric chain which is responsible for its translation and rotation movements and also for the shear

strain. The viscosity coefficient will be corresponding to this segmental movement of the polymeric chain. Under the action of a velocity gradient  $g$  of the hydrodynamic flow the polymeric m-ball performs the rotary movement also giving the endowment into the frictional component of the viscosity. In accordance with the superposition principle the segmental movement and the external rotary movement of the polymeric chains will be considered as the independent ones. In this case the external rotary movement of the polymeric chains without taking into account the segmental one is similar to the rotation of m-ball with the frozen equilibrium conformation of the all m polymeric chains represented into m-ball. This corresponds to the inflexible Kuhn's wire model [22]. The viscosity coefficient will be corresponding to the external rotating movement of the m-ball under the action of  $g$ . The all listed movement forms are enough in order to describe the diluted solutions. However, in a case of the concentrated solutions it is necessary to embed one more movement form, namely, the transference of the twisted between themselves polymeric chain one respectively another in m-ball. Exactly such relative movement of the polymeric chains contents into itself the all possible linkages effects. Accordingly to the superposition principle the polymeric chains movement does not depend on the above-listed movement forms if it doesn't change the equilibrium conformation of the polymeric chains in m-ball. The endowment of such movement form into let us note via  $\eta_{rel}$ . Not all the listed movement forms give the essential endowment into the  $\eta$ , however for the generality let us start from the taking into account of the all forms. In such a case the frictional component of a viscosity should be described by the expression:  $\eta = \eta_{ext} + \eta_{rel}$ , (18) or  $\eta = \eta_{ext} + \eta_{rel}$ , (19) here is the volumetric part of the polymer into solution. It is equal to the volumetric part of the monomeric links into m-ball; that is why it can be determined by the ratio:  $\eta_{rel} = \eta_{ext} \cdot \frac{V_{rel}}{V_{ext}}$ , (20) in which is the partial-molar volume of the monomeric link into solution. Combining the eq. eq. (9)-(14) and eq. (20) we will obtain:  $\eta = \eta_{ext} \cdot \frac{V_{rel}}{V_{ext}}$ . (21) The ratio of should be near to the density of the liquid monomer. Assuming of this approximation, we have:  $\eta = \eta_{ext} \cdot \frac{V_{rel}}{V_{ext}}$ . (22) At the rotation of m-ball under the action of  $g$  the angular rotation rate for any polymeric chain is the same but their links depending on the remoteness from the rotation center will have different linear movement rates. Consequently, in m-ball there are local velocity gradients of the hydrodynamic flow. Let  $g_{local}$  represents the averaged upon m-ball local velocity gradient of the hydrodynamic flow additional to  $g$ . Then, the tangential or strain shear formed by these gradients and at the rotation movement of m-ball in the medium of a solvent will be equal to:  $\gamma = g_{local} \cdot r$ . (23) However, the measurable strain shear correlates with the well-known external gradient  $g$  that gives another effective viscosity coefficient:  $\eta_{eff} = \eta_{ext} \cdot \frac{g_{local}}{g}$ . (24) Comparing the eq. (23) and eq. (24) we will obtain  $\eta_{eff} = \eta_{ext} \cdot \frac{g_{local}}{g}$ . (25) Noting (26) instead of the eq. (19) we will write (27) The endowment of the relative movement of twisted polymeric chains in m-ball into the frictional component of the viscosity should be in general case depending on a number of the contacts between monomeric links independently to which polymeric chain these links belong. That is why we assume:  $\eta_{rel} = \eta_{ext} \cdot \frac{g_{local}}{g}$ . (28) The efficiency of these contacts or linkages let us estimate

comparing the characteristic times of the rotation (shear) of m-ball into concentrated solution and polymeric ball into diluted solution determined by the expressions (16) and (17). Let's note that in accordance with the determination done by author [17] is the characteristic time not only for m-ball rotation, but also for each polymeric chain in it. Consequently, is the characteristic time of the rotation of polymeric chain twisted with others chains whereas is the characteristic time of free polymeric chain rotation. The above-said permits to assume the ratio as a measure of the polymeric chains contacts or linkages efficiency and to write the following in accordance with the (16) and (17): (29) Taking into account the (22) and combining the (28) and (29) into one expression we will obtain: (30) Here the coefficient of proportionality includes the ratio , which should considerably weaker depends on and N that the value . Substituting the (30) into (27) with taking into account the (22) we have: (31) Let us estimate the endowment of the separate terms in eq. (31) into . In accordance with Table 1 under conditions of our experiments the frictional component of the viscosity is changed from the minimal value  $\gg 4 \times 10^{-2} \text{ Pa}\cdot\text{s}$  to the maximal one  $\gg 6,5 \text{ Pa}\cdot\text{s}$ . Accordingly to the reference data the viscosity coefficient of the toluene has the order  $5 \times 10^{-4} \text{ Pa}\cdot\text{s}$ . The value of the viscosity coefficient representing the segmental movement of the polymeric chains estimated by us upon of the diluted solution of polystyrene in toluene consists of the value by  $5 \times 10^{-3} \text{ Pa}\cdot\text{s}$  order. Thus, it can be assumed , and it can be neglected the respective terms in eq. (31). With taking into account of this fact, the eq. (31) can be rewritten in a form convenient for the graphical test: . (32) On Fig. 4 it is presented the interpretation of the experimental values of into coordinates of the equation (32). Fig. 4 - An interpretation of the experimental data of  $\eta f$  in coordinates of the equation (32) At that, it were assumed the following values:  $M = 104,15 \text{ g/mole}$ ,  $a = 1,86 \times 10^{-10} \text{ m}$  under determination of accordingly to eq. (11) and  $\text{g/m}^3$  for liquid styrene. As we can, the linear dependence is observed corresponding to eq. (32) at each temperature; based on the tangent of these straight lines inclination (see the regression equations on Fig. 4) it were found the numerical values of , the temperature dependence of which is shown on Fig. 5 into the Arrhenius' coordinates. It is follows from these data, that the activation energy regarding to the movement of twisted polymeric chains in toluene is equal to  $39,9 \text{ kJ/mole}$ . It can be seen from the Fig. 4 and from the represented regression equations on them, that the values are so little (probably,  $\text{Pa}\cdot\text{s}$ ) that they are located within the limits of their estimation error. This, in particular, didn't permit us to found the numerical values of the ratio . So, the analysis of experimental data, which has been done by us, showed that the main endowment into the frictional component of the effective viscosity of the concentrated solutions "polystyrene in toluene" has the separate movement of the twisted between themselves into m-ball polymeric chains. Exactly this determines a strong dependence of the on concentration of polymer into solution and on the length of a chain . Fig. 5 - Temperature dependence of the viscosity coefficient in coordinates of the Arrhenius equation Elastic component of the effective viscosity It is follows from the data of

Table 1, that the elastic component of viscosity is a strong increasing function on polymer concentration, on a length of a chain  $N$  and a diminishing function on a temperature  $T$ . The elastic properties of the conformational state of the  $m$ -ball of polymeric chains are appeared in a form of the resistance to the conformational volume deformation under the action of the external forces. In particular, the resistance to the shear is determined by the shear modulus, which for the  $m$ -ball was determined by the expression (15). As it was shown by author [17], the elastic component of the viscosity is equal to: . (33) The factor of form depends on the deformation degree of the conformational volume of a ball [17, 21]. Combining the (15) and (16) into (33) and assuming we will obtain . (34) Comparing the (16) and (34) we can see, that the known from the reference data ratio is performed but only for the elastic component of a viscosity. It follows from the expression (34), that the parameters and are inseparable; so, based on the experimental values of (see Table 1) it can be found the numerical values only for the composition. The results of calculations are represented in Table 2. In spite of these numerical estimations scattering it is overlooked their clear dependence on  $T$ , but not on  $N$ . Table 2 - Calculated values  $L\tau$ ,  $\tau/L$ ,  $\tau$  and  $L$  based on the experimental magnitudes  $\eta_e$  and  $b$

$\rho \cdot 10^{-5}, \text{g/m}^3$	4,0	5,0	7,0	$\tau \cdot 10^{10}, \text{s}$	$L \cdot T, \text{OC}$	$M \cdot 10^4, \text{g/mole}$	5,1	4,1	3,3	2,2	5,1	4,1	3,3	2,2	5,1	4,1	3,3	2,2	25
$(L\tau)\eta_e \cdot 10^{10}, \text{s}$	2,63	3,14	2,72	2,99	1,71	1,72	2,61	4,25	1,15	1,29	1,57	4,00	$(\tau/L)b \cdot 10^{10}, \text{s}$	3,25	1,81	2,54	0,89	1,17	3,43
$1,91$	2,06	1,98	1,86	1,38	2,29	$\tau \cdot 10^{10}, \text{s}$	2,92	2,38	2,63	1,63	1,41	2,43	2,23	2,96	1,51	1,61	1,47	3,03	2,19
$L$	0,90	1,32	1,03	1,83	1,21	0,71	1,17	1,44	0,76	0,86	1,07	1,32	1,13	30	$(L\tau)\eta_e \cdot 10^{10}, \text{s}$	1,75	2,41	2,03	1,96
0,88	1,17	1,54	3,83	0,60	0,75	1,21	2,63	$(\tau/L)b \cdot 10^{10}, \text{s}$	2,10	1,56	1,81	0,82	0,87	1,94	1,39	1,73	1,00	1,62	1,22
2,11	$\tau \cdot 10^{10}, \text{s}$	2,17	1,94	1,92	1,27	0,88	1,51	1,46	2,57	0,78	0,98	1,21	2,56	1,59	$L$	0,81	1,24	1,00	1,55
1,00	0,78	1,05	1,49	0,78	0,60	1,00	1,12	1,04	35	$(L\tau)\eta_e \cdot 10^{10}, \text{s}$	1,09	1,62	1,67	1,61	0,60	0,53	0,67	2,58	0,51
0,60	1,02	2,04	$(\tau/L)b \cdot 10^{10}, \text{s}$	1,01	1,16	1,67	0,59	0,79	0,98	1,21	1,65	0,81	1,35	1,09	1,75	$\tau \cdot 10^{10}, \text{s}$	1,05	1,37	1,67
0,97	0,70	0,72	0,90	2,06	0,64	0,90	1,05	1,89	1,16	$L$	1,04	1,18	1,00	1,65	0,87	0,73	0,74	1,25	0,79
0,67	0,97	1,08	1,00	40	$(L\tau)\eta_e \cdot 10^{10}, \text{s}$	0,72	0,78	1,03	0,96	0,43	0,44	0,43	1,40	0,29	0,46	0,75	1,46	$(\tau/L)b \cdot 10^{10}, \text{s}$	0,70
1,01	1,54	0,39	0,73	0,62	1,00	0,90	0,54	0,92	0,91	1,31	$\tau \cdot 10^{10}, \text{s}$	0,71	0,89	1,26	0,61	0,56	0,52	0,66	1,12
0,40	0,65	0,83	1,38	0,80	$L$	1,01	0,88	0,82	1,57	0,77	0,84	0,66	1,25	0,73	0,71	0,91	1,06	0,93	Parameter $b$

In accordance with the determination (6), the  $b$  parameter is a measure of the velocity gradient of hydrodynamic flow created by the working cylinder rotation, influence on characteristic time of action on the shear strain of the  $m$ -ball and its rotation movement. Own characteristic time of  $m$ -ball shear and rotation accordingly to (16) depends only on  $N$  and  $T$  via . It follows from the experimental data (see Table 1) that the  $b$  parameter is a function on the all three variables  $N$  and  $T$ , but, at that, is increased at  $T$  increasing and is decreased at  $N$  increasing. In order to describe these dependences let us previously determine the angular rate ( $\text{s}^{-1}$ ) of the strained  $m$ -ball rotation with the effective radius of the



working cylinder by diameter  $d$  contracting with the surface: (35) Here is appeared due to the difference in the dimensionalities of  $\tau$  and  $\lambda$ . Let us determine the  $\lambda$  as the reverse one: (36) Accordingly to (36) is a time during which the m-ball with the effective radius under the action of working cylinder by diameter  $d$  rotation will be rotated on the angle equal to the one radian. Let us note, that the  $\lambda$  was determined by authors [17] also in calculation of the m-ball turning on the same single angle. Since in our experiments the working cylinder had two rotating surfaces with the diameters  $d_1$  and  $d_2$ , the value was averaged out in accordance with the condition  $d = (d_1 + d_2)/2$ ; so, respectively, the value was averaged out too:  $\lambda$ . (37) So,  $\lambda$  is in inverse proportion to  $\omega$ ; therefore through the constant device it is in inverse proportion to  $\dot{\phi}$ . However, as it was noted, in m-ball due to the difference in linear rates of the polymeric chains links it is appeared the hydrodynamic interaction which leads to the appearance of the additional to local averaged upon m-ball velocity gradient of the hydrodynamic flow  $\dot{\gamma}$ . This local gradient acts not on the conformational volume of the m-ball but on the monomeric framework of the polymeric chains (the inflexible Kuhn's wire model [22]). That is why the endowment of  $\tau$  into characteristic time depends on the volumetric part of the links into the conformational volume of m-ball, i. e.  $\tau \propto V$ . Therefore, it can be written the following:  $\tau = \tau_0 V$ , (38) that with taking into account of eq. (37) leads to the expression  $\tau = \tau_0 V \dot{\phi}$ . (39) Combining the (16) and (39) into (6) we will obtain  $\tau = \tau_0 V \dot{\phi} = \tau_0 V \omega r$ . (40) As we can see, here the parameters  $\tau_0$  and  $r$  are also inseparable and can not be found independently one from another. That is why based on the experimental data presented in Table 1 it can be found only the numerical values of the ratio  $\tau_0 r$ . After the substitution of values  $a = 1,86 \times 10^{-10}$  m,  $d_1 = 3,4 \times 10^{-2}$  m,  $d_2 = 3,3 \times 10^{-2}$  m we have  $\tau_0 r = 25$ . (41) As it was marked, we could not estimate the numerical value of  $\tau_0$  due to the smallness of the value lying in the error limits of its measuring. That is why, we will be consider the ratio as the fitting parameter starting from the consideration that the concentrated solution for polymeric chains is more ideal than the diluted one and, moreover, the m-ball is less strained than the single polymeric ball. That is why, was selected in such a manner that the factor of form was near to the 1. This lead to the value  $\tau_0 r = 25$ . The calculations results of accordingly to equation (41) with the use of experimental values from Table 1 and also the values  $\tau_0 r = 25$  are represented in Table 2. They mean that the  $\tau$  is a visible function on a temperature but not on  $a$  and  $N$ . On a basis of the independent estimations of  $\tau$  and it was found the values of  $\tau_0$  and  $r$ , which also presented in Table 2. An analysis of these data shows that with taking into of their estimation error it is discovered the clear dependence of  $\tau$  and  $L$  on  $T$ , but not on  $a$  and  $N$ . Especially clear temperature dependence is visualized for the values  $\tau$ , obtained via the averaging of  $\tau$  at giving temperature for the all values of  $a$  and  $N$  (Table 2). The temperature dependence of  $\tau$  into the coordinates of the Arrhenius' equation is presented on Figure 6. Fig. 6 - Temperature dependence of the average values of the characteristic time  $\tau$  of the segmental movement of polymeric chain in coordinates of the Arrhenius equation

Conclusions Investigations of a gradient dependence of the effective viscosity of concentrated solutions of

polystyrene permitted to mark its frictional  $\eta_f$  and elastic  $\eta_e$  components and to study of their dependence on a length of a polymeric chain  $N$ , on concentration of polymer  $\rho$  in solution and on temperature  $T$ . It was determined that the main endowment into the frictional component of the viscosity has the relative motion of the intertwined between themselves in m-ball polymeric chains. An efficiency of the all possible gearings is determined by the ratio of the characteristic times of the rotation motion of intertwined between themselves polymeric chains in m-ball and Flory ball. This lead to the dependence of the frictional component of viscosity in a form for concentrated solutions, which is agreed with the experimental data. It was experimentally confirmed the determined earlier theoretical dependence of the elastic component of viscosity for concentrated solutions, that is lead to the well-known ratio, which is true, however, only for the elastic component of the viscosity. On a basis of the experimental data of  $\eta_e$  and  $b$  it were obtained the numerical values of the characteristic time  $\tau_m$  of the segmental motion of polymeric chains in concentrated solutions. As the results showed,  $\tau_m$  doesn't depend on  $N$ , but only on temperature. The activation energies and entropies of the segmental motion were found based on the average values of  $\tau_m$ . An analysis which has been done and also the generalization of obtained experimental data show, that as same as in a case of the low-molecular liquids, an investigation of the viscosity of polymeric solutions permits sufficiently accurately to estimate the characteristic time of the segmental motion on the basis of which the diffusion coefficients of the polymeric chains in solutions can be calculated; in other words, to determine their dynamical characteristics.