Introduction The viscosity h 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 h value, also by a wide diapason (from 10–3 to 102 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 h for the concentrated solutions is considerable stronger than the h 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 h0 and the final h¥ viscosities (h0>h¥), to which the extreme conditions g ® 0 and g ® ¥ correspond respectively. Due to dependence of η 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 η0, which is formally determined as the limited value at g→0. Exactly this value η0 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 η0. 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 h on the length N of a polymeric chain and on the concentration r (g/m3) of a polymer in solution exists: with the indexes α = 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 h 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 h 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>>1 = x–g, g = 0,8. Hence, both expressions (3) and (4) declare the gradient dependence of h by the function of the one non–dimensional parameter gt*. However, under the theoretical estimation of h 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 h 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 0,4×105; 0,5×105 and 0,7×105 g/m3 for the four fractions of polystyrene characterizing by the apparent molar weights M = 5,1×104; M = 4,1×104; M = 3,3×104 and M = 2,2×104 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 viscosity for the polystyrene melt were investigated using the same fractions at 210 0C. Temperature dependence of the polystyrene melt was investigated for the fraction with average molecular weight M = 2,2×104 g/mole under three temperatures, namely 190, 200 and 210 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 d1 = 3,4×10–2 and d2 = 3,9×10–2 m in a case of the concentrated solutions of polystyrene investigation and using the device by «cone-plate» type equipped with the working cone by 0,30 angle and radius r = 1,8×10-2 m in a case of the polystyrene melt investigation. Polystyrene’s melt Experimental data Typical dependencies of the melt viscosity η on the angular rate ω (rotations per second) of the working cone rotation are represented on Figures 1 and 2. In order to analyze the experimental curves of η(ω), the equation (5) [20] with the same remarks as to the numerical estimations of parameters ηe, ηf and b was used. As it can be seen from the Figures 1 and 2, calculated curves of η(ω) accordingly to the equation (5) [20] with the founded parameters ηf, ηe and b describe the experimental data very well. Results of the numerical estimations of ηf, ηe та b on a length of the polymeric chain at 210 0C are represented in Table 1 and the temperature dependencies are represented in Table 2. Review of these data shows, that the all three parameters are the functions on the length of a chain and on temperature. But at this, ηe and ηf are increased at N increasing and are decreased at T increasing, whereas b parameter is changed into the opposite way. Fig. 1 - Experimental (points) and calculated in accordance with the equation (5) [20] (curves) dependencies of the effective viscosity on the velocity of the working cone rotation. T = 210 0C Fig. 2 - Experimental (points) and calculated in accordance with the equation (5) [20] (curves) dependencies of the

effective viscosity on the velocity of the working cone rotation. M = 2,2·104 g/mole Table 1 - Optimization parameters ηf, ηe and b obtained from the experimental data at T = 210 0C M·10-4, g/mole ηf, Pa·s ηe, Pa·s b, s-1 5.1 18.49 7.09 0.0019 4.1 10.58 3.19 0.0025 3.3 6.50 2.65 0.0096 2.2 3.69 0.55 0.0169 Table 2 - Optimization parameters ηf, ηe and b obtained from the experimental data for polystyrene with M = 2,2·104 g/mole T, 0C ηf, Pa·s ηe, Pa·s b, s-1 190 10.60 2.50 0.0045 200 7.76 1.40 0.007 210 3.69 0.55 0.0169 Frictional component of the effective viscosity of melt Results represented in Table 1 and Table 2 show that the frictional component of the viscosity ηf very strongly depends on the length of the polymeric chains and on the temperature. The whole spectrum of the dependence of ηf on N and T will be considered as the superposition of the above earlier listed three forms of the motion which make the endowment into the frictional component of the viscosity of melt, namely the frictional coefficients of viscosity ηsm, ηpm and ηpz [20]. Not the all listed forms of the motion make the essential endowment into ηf, however for the generalization let us start from the taking into account of the all forms. So, the frictional component of the viscosity should be described by the expression (19) [20], but for the melt it is necessary to accept that ηs = 0, and φ = 1. . (5) In a case of the melts ηpz is determined by the equations (30) [20], but at . (6) Here the coefficient of the proportionality contains the ratio , however, since the melt is the ideal solution for polymer, that is why it can be assumed that Lm = 1. By substituting of the (6) into (40) [20], we will obtain (7) Let’s estimate an endowment of the separate components into ηf. The results represented in Table 1 show, that under conditions of our experiments the frictional component of viscosity is changed from the minimal value ≈ 3,7 Pa·s till the maximal one equal to ≈ 18,5 Pa·s. The value of the viscosity coefficient ηsm, which represents the segmental motion of the polymeric chains and estimated [21] on the basis of ηf for diluted solution of polystyrene in toluene is equal approximately 5·10-3 Pa·s. Thus, it can be assumed that ηsm ηf and to neglect by respective component in (7). Taking into account of this fact, the expression (7) let’s rewrite as follow: . (8) For the melts , that is why the interpretation of the experimental values of ηf as the function of N2 is represented on Figure 3. It can be seen from the Figure 3, that the linear dependence corresponding to the equation (8) is observed, and the numerical value of was found upon the inclination tangent of the straight line; under the other temperatures this coefficient was found using the experimental data from Table 2. For the estimation of it was assumed that g/m3, ρ0 was calculated in accordance with (11) [20] at M0 = 104,15 g/mole, a = 1,86·10-10 m. Fig. 3 - Interpretation of the experimental values of ηf in the coordinates of the equation (8) at T = 210 0C Temperature dependence of into coordinates of the Arrhenius equation is represented on Figure 4. Fig. 4 - Temperature dependence of the numerical estimations of in the coordinates of the Arrhenius equation So, an activation energy Epz, of the relative motion of intertwined polymeric chains into polystyrene’s melt consists of 106 ± 35 kJ/mole. It can be seen from the presented Figure 3 and from the regression equation,

that the values of are very little and are within the ranges of their estimation error; this cannot give the possibility to estimate the value of gm/g. So, as the analysis of the experimental data showed, the main endowment into the frictional component of the effective viscosity of the polystyrene’s melt has the relative motion of the intertwining between themselves into m-ball polymeric chains. Exactly this determines the dependence of ηf on the length of a chain (). Elastic component of the effective viscosity of melt It can be seen from the Table 1 and Table 2, that the elastic component of the viscosity ηe is strongly growing function on a length of a chain N and declining function on temperature T. The elastic component of the viscosity is described by the equation (6), but at Lm = 1. (9) Correspondingly, instead of the (34) [20] we obtained (10) Using the expression (10) and the experimental values of ηe (see Table 1 and Table 2) it was found the numerical values of the characteristic time of the segmental motion τm. The results of calculation are represented in Table 3 and Table 4. Despite the disagreement in numerical estimations, it is observed their dependence on T, but not on the N; this fact is confirmed by the expression (10). Table 3 - Characteristic times of the segmental motion calculated based on the experimental values of ηe and b (M = 2.2·104 g/mole) T, 0C (τm)ηe·1011, s (τm)b·1011, s τm·1011, s 190 6.86 5.50 6.18 200 3.76 3.58 3.67 210 1.45 1.48 1.47 Table 4 - Characteristic times of the segmental motion calculated based on the experimental values of ηe τa b (T = 210 0C) M·10-4, g/mole (τm)ηe·1011, s (τm)b·1011, s τm·1011, s 5.1 1.11 1.70 1.48 4.1 1.05 2.25 3.3 1.84 0.99 2.2 1.45 1.48 Parameter b In accordance with the determination (6) [20], the b parameter is a measure of the velocity gradient of hydrodynamic flow created by the working cone 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) [20] depends only on N and T via . It is follows from the experimental data (see Table 1 and Table 2) that the b parameter is a function of N and T, but at this it is increased at T increasing and is decreased at N growth. In order to describe of these dependencies let’s previously determine the angular rate (s-1) of the rotation of m-ball with the effective radius Rm, which contacts with the surface of the working cone with radius r (11) Here π is appeared as a result of the different units of the dimention and . Let’s determine the as the reverse one to the (12) In equation (12) is a time during which the m-ball with the conformational radius Rm under the action of working cone rotation with radius r will be rotated on the angle equal to the one radian. Let us note, that the was determined by authors [17] also in calculation of the m–ball turning on the same single angle. Thereby, is inversely proportional to ω, so via the constant of the device is inversely proportional to g: . However, into m-ball as a result of the difference in the linear rates of the links of polymeric chains under their rotation the hydrodynamic interaction is appeared, which leads to the appearance of the additional to the g local averaged upon m-ball gradient velocity of the hydrodynamic flow gm. This local gradient gm acts not on the conformational volume of m-ball, but on the monomeric

frame of the polymeric chains (the inflexible Kuhn's wire model [23]). That is why the endowment of into characteristic time depends on the volumetric part of the links into the conformational volume of m–ball, i. e. . Into the melt φ = 1, therefore, it can be written the following: , (13) that leads with taking into account of the (12), to the expression . (14) By combining of the (16) [20] and (14) in (6) [20], we obtained . (15) As we can see, using the experimental values of b parameter (see Table 1 and Table 2) it can be calculated . After the substitution of the values a = 1.86·10-10 m, r = 1,8·10-2 m, we obtained . (16) Numerical value of the ratio was considered as a parameter, which selected in such a way, that calculated accordingly to (16) values of corresponded to the calculated values accordingly to (10). So, the obtained value of = 39. The results of calculations of and , are compared in Tables 3 and 4. As the results show, and is visible function on the temperature but not on the N. That is why based on the data of Tables 3 and 4 it were calculated the averaged values of the of the characteristic time of segmental motion of the macromolecule. Temperature dependence of into coordinates of the Arrhenius equation is represented on Figure 5. Fig. 5 - Temperature dependence of the averaged values of characteristic time τ of the segmental motion of polymeric chain into coordinates of the Arrhenius equation Characteristic time of the segmental motion of polystyrene in solutions and melt The presentation of values into Arrhenius' coordinates equation (Fig. 6) [20] and (Fig. 5) permitted to obtain the expressions for concentrated solutions and melt, respectively: , (17) , (18) For diluted solution of polystyrene in toluene it was early obtained [21]: , (19) On a basis of the equations (17) - (19) it was calculated the activation energies of the segmental motion of polystyrene in diluted, concentrated solutions and melt, which consists of 55,4; 49,4 and 133.0 kJ/mole, respectively. Characteristic time τ can be obtained by equation of the theory of absolute reactions rates [16]: , (20) where is an activation energy of the segmental motion; is an activation entropy of the segmental motion. By comparing the expression (20) and experimental data (17) - (19), it was found for solutions at t = 30 ºC and for melt at t = 200 ºC the values of the activation entropy = 15,3; 13,5 and 28,8 respectively. As we can see, the difference between energies and entropies of activation in diluted and concentrated solutions is little and is in a range of the error of their estimation. At the same time, indicated parameters into melt of the polystyrene is approximately in two times higher. Besides, the growth of the activation entropy does not compensate the activation energy growth; as a result, the characteristic time of the segmental motion into melt is on 2-3 orders higher, than into the solutions (at the extrapolation of τ on general temperature). Let’s compare the values of the activation energies E with the evaporation heats ΔHevap of styrene (-43,94 kJ/mole) and toluene (–37,99 kJ/mole). So, independently on fact, which values of ΔHevap were taken for styrene or toluene, it is observed a general picture: Eτm, Eτf > ΔHвип. It is known [24], that for the low-molecular liquids, viscosity of which is determined by the Brownian or translational form of the molecules motion, the activation energy of the viscous flow is in 3-4 times

less than the evaporation heats. This points on fact, that the segmental motion which is base of the reptation mechanism of the polymeric chains motion, is determined by their deformation-vibrational freedom degrees. However, let’s mark another circumstance. During the study of the bimolecular chains termination kinetics [25] which is limited by their diffusion, in polymeric matrixes of the dimethacrylate TGM-3 (triethylenglycole dimethacrylate), monomethacrylate GMA (2,3--epoxypropylmethacrylate) and their equimolar mixture TGM-3 : GMA = 1 : 1 in the temperature range 20 ÷ 70 ºC it were obtained the following values of the activation energies: 122,2, 142,3 and 131,0 kJ/mole. Since the diffusion coefficient of the macroradical is also determined by the characteristic time of the segmental motion, it can be stated that the presented above activation energies of the segmental motion in melt and polymeric matrix are good agreed between themselves. A sharp their difference from the activation energy into solutions points on: firstly, a great influence of the solvent as a factor activating the segmental motion of polymeric chain, and secondly, on fact, that the dynamic properties of the polymeric chains in melt are very near to their dynamic properties in polymeric matrix. Dynamic properties of polystyrene in solutions and melt Dynamical properties of the polymeric chains are determined by characteristic times of their translational motion () and rotation () motions. As it was noted earlier, the characteristic time of the shear strain is also equal to . Since the monomeric links connected into a chain, the all of these types of motion are realized exceptionally in accordance with the reptation mechanism, that is via the segmental motion with the characteristic time τs. That is why, let’s analyze and generalize once more the obtained experimental data of the characteristic times of the segmental motion of the chains of polystyrene in solutions and melts, which were estimated based on elastic component of the viscosity and parameter b. Besides, let’s add to this analysis the characteristic times of the segmental motion, estimated based on coefficient of the frictional component of viscosity of diluted solution (), concentrated solution and melt (). The values will be used in the sequel for the estimation of the characteristic time of the translation motion and of the coefficient of the diffusion D of the polystyrene chains into solutions and melt. Accordingly to the experimental data the temperature dependence , estimated based on the elastic component of the viscosity and parameter b, is described by the equations: in diluted solution (temperature range 20 - 35 ºC) , (21) in concentrated solution (temperature range 25 - 40 ºC) , (22) in melt (temperature range 190 - 210 ºC) (23) Let’s write also the temperature dependencies of the coefficients of a frictional component of the viscosity: in diluted solution , (24) in concentrated solution , (25) in melt . (26) Next, let’s use the proposed earlier expression for characteristic time of the segmental motion in the following form , (27) where -28,78 and -29,22 at T = 303 K and T = 473 K correspondingly. Using of these values and comparing (27) and (21) - (23), we will obtain the numerical estimations for the activation entropy of the segmental motion , which represented in Table 5. In Table 5 also the activation energies of the segmental

motion and the value at T = 303 K and T = 473 K are represented too. Values at T = 303 K in melt were obtained by the extrapolation of expression (20) on given temperature, at which melt is in the solid glass-like state. Table 5 - Characteristic parameters of segmental motion of polystyrene in solutions and melt System Es, kJ/mole Epz, kJ/ mole T = 303 K T = 473 K , s , s , s , s Diluted solutions 55,3 15,3 –– –– 2,5× 10-10 –– –– –– Concentrated solutions 49,4 13,5 39,9 6,0 1,5× 10-10 6,0× 10-9 –– 1,9× 10-11 Melt 133,1 28,8 105,9 17,0 5,6× 10-3* 1,5× 10-2* 3,1× 10-11 4,0× 10-9 Note. *Data found by the extrapolation accordingly to the equations (23) and (34) in the field of the glass-like state of melt It can be seen from the Table 5, that the numerical values both of , and the thermodynamic characteristics (and) of the segmental motion into diluted and concentrated solutions are differed only within the limits of the experimental error of their estimations. In melt these values are essentially differed. At this, the growth of the activation energy (approximately from 55 kJ/mole till 133 kJ/mole) of the segmental motion is not compensated by the growth of the activation entropy (till); as a result, the values of in melt are on two orders greater than in solutions (at T = 473 K) and on six orders greater at T = 303 K. Let’s assume, that the coefficients of the frictional component of the viscosity of polymeric chains are described by as same general expression [16], as the coefficients of the viscosity of low-molecular solution. At that time it can be written: , (28) , (29) where V is the partial-molar volume of the monomeric link of a chain. and are per sense, the characteristic times of the segmental motion of free polymeric chain into diluted solution and overlapping one with others polymeric chains into the concentrated solution and melt taking into account the all possible gearing effects, correspondingly. Since the partial-molar volume V of the monomeric link of the polystyrene is unknown, then for the next calculations it can be assumed without a great error to be equal to the molar volume of the monomeric link into the melt: , (30) where g/m3 is a density of the polystyrene melt; M0 = 104.15 g/mole is the molar mass of styrene. Let us write (28) and (29) in general form: . (31) At this 18,15 and 18,59 at T = 303 K and T = 473 K, correspondingly. Taking into account of this value and comparing the (31) and (24) and (25) and (26), we will obtain the temperature dependences and : for diluted solution , (32) for concentrated solution , (33) for melt . (34) On the basis of two last ones expressions the have been calculated at T = 303 K and T = 473 K. Taking into account a general equation (27) it has been found also the value of the activation entropy (see Table 5). Comparing the parameters of the equation (21) for and (32) for , it can be seen, that the difference between them is adequately kept within the error limits of their estimation. The values of and at T = 303 K, equal to s and s correspondingly prove of this fact. Thus, it can be assumed that , and that is why the coefficient of the frictional component of the viscosity of the polymeric chains can be described by as same general expression (28) as for the coefficient of the low-molecular solution. The values of calculated accordingly to the expressions (34) and (35) for concentrated solution at T = 303 K and melt at T = 473 K correspondingly (see

Table 5), are essentially differed from : , approximately on two orders. An analysis of the parameters of the equations (22), (23) and (33), (34) showed that the difference between and is caused by two factors, which abhorrent the one of the other: by insignificant decreasing of the activation energy (), that should be decreased the , and by a sharp decreasing of the activation entropy , that increases of . As it was said, the coefficient of the frictional component of viscosity in concentrated solutions and melt caused by the motion of the overlapping between themselves polymeric chains relatively the one of the other and characterizes the efficiency of the all possible gearings. However, the mechanism of this motion is also reptational that is realized via the segmental motion. Correspondingly, between the times and the some relationship should be existing. Let’s assume the thermodynamical approach for the determination of this relationship as a one among the all possible. Let’s determine the notion «gearing» as the thermodynamical state of a monomeric link of the chain, at which its segmental motion is frozen. This means, that under the relative motion of the intertwining between themselves polymeric chains the reptational mechanism of the transfer at the expense of the segmental motion takes place, but under condition that the part of the monomeric links of a chain is frozen. Let the is a standard free energy of the monomeric link transfer from a free state into the frozen one. Then the probability of the frozen states formation or their part should be proportional to the value . That is why, if the is a constant rate of the free segmental transfer, and is the rate constant of the frozen segmental transfer, then between themselves the relationship should be existing: . (35) Then , additionally to , has a free activation energy equal to the standard free defrosting energy of the frozen state. Since , , we obtained . (36) By assigning (37) and taking into account the experimentally determined ratios , and , we conclude, that in (37) , and , and besides the entropy factor should be more upon the absolute value than the enthalpy factor . These ratios per the physical sense are sufficiently probable. A contact of the links under the gearing can activates a weak exothermal effect at the expense of the intermolecular forces of interaction, and the frosting of the segmental movement activates a sharp decrease of the entropy of monomeric link , but at this . Let’s rewrite the (36) with taking into account of (37) in a form . (38) Comparing the expressions (22) and (33), (23) and (35) and taking into account (38) we obtained: for concentrated solution kJ/mole, kJ/mole, , for melt kJ/mole, kJ/mole, . In connection with carried out analysis the next question is appeared: why in the concentrated solutions and melt the gearing effect hasn’t an influence on the elastic component of viscosity , and determined based on this value characteristic time of the segmental motion is ; at the same time, the gearings effect strongly influences on the frictional component of viscosity, on the basis of which the is estimated. Probably, the answer on this question consists in fact that the elastic component of the viscosity is determined by the characteristic time of the shear which is equal to the characteristic time of rotation. Accordingly to the superposition principle the rotation motion of the m-ball of the intertwining between

themselves polymeric chains can be considered independently on their mutual relocation, that is as the rotation with the frozen conformation. As a result, the gearings effects have not an influence on the characteristic time of the rotation motion. Free segmental motion gives a contribution in a frictional component of viscosity, but it is very little and is visible only in the diluted solutions. That is why even a little gearing effect is determining for the frictional component of viscosity in concentrated solutions and melts. Let’s use the obtained numerical values of the characteristic times of the segmental movement for the estimation of dynamical properties of the polystyrene chains that is their characteristic time of the translational movement and coefficient of diffusion D into solutions and melt. Accordingly to [26], the values and D are determined by the expressions: in diluted solutions , (39) . (40) in concentrated solutions and melt , (41) . (42) In order to illustrate the dynamic properties of the polystyrene in solutions and melt in Table 6 are given the numerical estimations of the characteristic times of segmental and translational motions of the polystyrene and diffusion coefficients D. It was assumed for the calculations m, N = 103 and g/m3 for concentrated solution and melt correspondingly. As we can see, the characteristic time of the translational motion of the polystyrene chains is on 4 and 6 orders higher than the characteristic time of their segmental motion; this is explained by a strong dependence of on the length of a chain. The coefficients of diffusion weakly depend on the length of a chain, that is why their values into solutions is on 2-3 order less, than the coefficients of diffusion of low-molecular substances, which are characterized by the order 10-9 m2/s. A special attention should be paid into a value of the diffusion coefficient at T = 303 K in a field of the glass-like state of melt m2/s. Let’s compare of this value D with the diffusion coefficients of the macroradicals in polymeric matrixes TGM-3, TGM-3-GMA and GMA which estimated experimentally [25] based on the kinetics of macroradicals decay, which under the given temperature consist of m2/s. Table 6 - Dynamic characteristics of polystyrene in solutions and melt System T = 303 K T = 473 K , s , s D, m2/sc , s , s D, m2/s Diluted solutions 2,0× 10-10 1,3× 10-6 1,4× 10-12 –– –– –– Concentrated solutions 2,0× 10-10 2,9× 10-4 1,0× 10-13 –– –– –– Melt 5,0× 10-3* 7,2× 10-3* 7,3× 10-22* 3,0× 10-11 4,3× 10-5 1,2× 10-13 Note. *Data found by the extrapolation in a field of the glass-like state of melt. Thus, carried out analysis shows, that the studies of the viscosity of polymeric solutions permits sufficiently accurately to estimate the characteristic times of the segmental and translational movements, on the basis of which the coefficients of diffusion of polymeric chains into solutions can be calculated. Conclusions Investigations of a gradient dependence of the effective viscosity of polystyrene melt permitted to mark its frictional ηf and elastic ηe components and to study of their dependence on a length of a polymeric chain N, on concentration of polymer ρ 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 melt, which is agreed with the experimental data. It was experimentally confirmed the determined earlier theoretical dependence of the elastic component of viscosity for the melt , 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 ηe and b it were obtained the numerical values of the characteristic time τm of the segmental motion of polymeric chains in melt. As the results showed, τm 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 . In a case of a melt the value of E and is approximately in twice higher than the same values for diluted and concentrated solutions of polystyrene in toluene; that points on a great activation action of the solvent on the segmental motion of the polymeric chain, and also notes the fact that the dynamical properties of the polymeric chains in melt is considerably near to their values in polymeric matrixes, than in the solutions. 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 melt can be calculated; in other words, to determine their dynamical characteristics