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Yu. G. Medvedevskikh, O. Yu. Khavunko, L. I. Bazylyak, G. E. Zaikov

VISCOELASTIC PROPERTIES OF THE POLYSTYRENE IN CONCENTRATED SOLUTIONS AND MELTS (PART 1)

Keywords: effective viscosity, frictional and elastic components of the viscosity, m–ball, segmental motion, activation energy.

A gradient dependence of the effective viscosity η for the concentrated solutions of the polystyrene in toluene at three concentrations ρ = 0,4·10^5; 0,5·10^5; 0,7·10^5 g/m^3 correspondingly for the fourth fractions of the polystyrene with the average molar weights M = 5,1·10^4; 4,1·10^4; 3,3·10^4; 2,2·10^4 g/mole respectively has been experimentally investigated. For every pair of the values ρ and M a gradient dependence of the viscosity was studied at four temperatures: 25, 30, 35 *and* 40°*C. An effective viscosity of the melts of polystyrene was studied for the same fractions, but at the temperatures* 190, 200 *and* 210°*C. The investigations have been carried out with the use of the rotary viscosimeter «Rheotest* 2.1*» under the different angular velocities ω of the working cylinder rotation. An analysis of the dependencies η(ω) permitted to mark the frictional η_f and elastic η_e components of the viscosity ant to study their dependence on temperature T, concentration ρ and on the length of a chain N. It was determined, that the relative movement of the intertwined between themselves polymeric chains into m–ball, which includes into itself the all possible effects of the gearings, makes the main endowment into the frictional component of the viscosity. The elastic component of the viscosity η_e is determined by the elastic properties of the conformational volume of the m–ball of polymeric chains under its shear strain. The numerical values of the characteristic time and the activation energy of the segmental movement were obtained on the basis of the experimental data. In a case of a melt the value of E and ΔS*/R are approximately in two times more than the same values for the diluted and concentrated solutions of the polystyrene in toluene; this means that the dynamic properties of the polymeric chains in melt are considerably near to their values in polymeric matrix than in solutions. Carried out analysis and generalization of the obtained experimental data show that as same as for low–molecular liquids the studying of the viscosity of polymeric solutions permits sufficient adequate to estimate the characteristic time of the segmental movement accordingly to which the coefficients of polymeric chains diffusion can be calculated in solutions and melt, in other words, to determine their dynamic characteristics.*

Ключевые слова: эффективная вязкость, фрикционный и упругий компоненты вязкости, клубок, сегментальная подвижность, энергия активации.

Экспериментально исследована зависимость градиента эффективной вязкости η для концентрированных растворов полистирола в толуоле при трех концентрациях ρ = 0,4·10^5; 0,5·10^5; 0,7·10^5 г/м^3 соответственно для четырех фракций полистирола со средними молярными массами M = 5,1·10^4; 4,1·10^4; 3,3·10^4; 2,2·10^4 г/моль соответственно. Для каждой пары значений ρ и M зависимость градиента вязкости изучалась при четырех температурах: 25, 30, 35 и 40°C. Эффективная вязкость расплавов полистирола была изучена для тех же фракций, но при температурах 190, 200 и 210°C. Исследования были проведены с использованием ротационного вискозиметра «Rheotest 2,1» при разных угловых скоростях ω вращения рабочего цилиндра. Анализ зависимостей η (ω) позволяет выделить фрикционный η_f и упругий компонент η_e вязкости и изучить их зависимость от температуры T, концентрации ρ и длины цепи N. Было установлено, что относительное движение переплетенных между собой полимерных цепей в клубке дает основной вклад в фрикционную составляющую вязкости. Упругий компонент вязкости η_e определяется упругими свойствами конформационного объема клубка полимерных цепей при деформации сдвига. На основе экспериментальных данных были получены численные значения характеристического времени и энергии активации сегментального движения. В случае расплава значение E и ΔS/R примерно в два раза больше тех же значений для разбавленных и концентрированных растворов полистирола в толуоле; это означает, что динамические свойства полимерных цепей в расплаве значительно ближе значениям этих свойств в полимерной матрице, чем в растворах. Проведенный анализ и обобщение полученных экспериментальных данных показывает, что так же, как и для низкомолекулярных жидкостей, изучение вязкости полимерных растворов позволяет достаточно адекватно оценить характеристическое время сегментальной подвижности, соответственно которому коэффициенты диффузии полимерных цепей могут быть рассчитаны в растворах и расплаве, другими словами, чтобы определить их динамические характеристики.*

Introduction

The viscosity η 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 η 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 η for the concentrated solutions is considerable stronger than the η 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 η_0 and the final η_∞ viscosities ($\eta_0 > \eta_\infty$), to which the extreme conditions $g \to 0$ and $g \to \infty$ 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 η_0, which is formally determined as the limited value at $g \to 0$. Exactly this value η_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 η_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 η on the length N of a polymeric chain and on the concentration ρ *(g/m^3)* of a polymer in solution exists: $\eta \sim \rho^{\alpha} N^{\beta}$ with the indexes $\alpha = 5 \div 7$, $\beta = 3{,}3 \div 3{,}5$, as it was shown by authors [4].

3. It was experimentally determined by authors [1, 5] that the viscosity η 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:

$$\eta \sim t^* \sim N^{\beta} \qquad (1)$$

with the index $\beta = 3{,}4$.

Among the numerous theoretical approaches to the analysis of the polymeric solutions viscosity anomaly, *i. e.* the dependence of η 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]:

$$\eta = E \cdot t^* \qquad (2)$$

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]:

$$(\eta - \eta_\infty)/(\eta_0 - \eta_\infty) = f(gt^*) \qquad (3)$$

It was greatly recognized the universal scaling ratio [1, 5]:

$$\eta = \eta_0 \cdot f(gt^*) \qquad (4)$$

in which the dimensionless function $f(gt^*) = f(x)$ has the asymptotes $f(0) = 1$, $f(x)_{x>>1} = x^{-\gamma}$, $\gamma = 0{,}8$.

Hence, both expressions (3) and (4) declare the gradient dependence of η by the function of the one non–dimensional parameter gt^*. However, under the theoretical estimation of η and t^* as a function of N there are contradictions between the experimentally determined ratio (1) and $\beta = 3{,}4$. Thus, the analysis of the entrainment of the surrounding chains under the movement of some separated chain by [12] leads to the dependencies $\eta \sim N^{3,5}$ but $t^* \sim N^{4,5}$. 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 $\eta \sim N^3$, $t^* \sim N^4$. The approach in [14] which is based on the conception of the reptational mechanism of the polymeric chain movement gives the following dependence $\eta \sim t^* N^3$. So, the index $\beta = 3{,}4$ 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 η 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 $0{,}4\cdot10^5$; $0{,}5\cdot10^5$ and $0{,}7\cdot10^5$ *g/m*^{3} for the four fractions of polystyrene characterizing by the apparent molar weights $M = 5{,}1\cdot10^4$; $M = 4{,}1\cdot10^4$; $M = 3{,}3\cdot10^4$ and $M = 2{,}2\cdot10^4$ *g/mole*. For each pair of values ρ 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 $d_1 = 3{,}4\cdot10^{-2}$ and $d_2 = 3{,}9\cdot10^{-2}$ *m*.

Results and discussion: concentrated solutions

Initial statements

Typical dependences of viscosity η of solution on the angular velocity ω *(turns/s)* of the working cylinder rotation are represented on *Fig.* 1–3. Generally it was obtained the 48 curves of $\eta(\omega)$.

For the analysis of the experimental curves of $\eta(\omega)$ it was used the expression [15, 20]:

$$\eta = \eta_f + \eta_e\left(1-\exp\{-b/\omega\}\right)/\left(1+\exp\{-b/\omega\}\right) \qquad (5)$$

in which η is the measured viscosity of the solution at given value ω of the working cylinder velocity rate; η_f, and η_e are frictional and elastic components of η;

$$b/\omega = t_v^*/t_m^* \qquad (6)$$

where t_m^* is the characteristic time of the shear strain of the conformational volume for *m*–ball of intertwined polymeric chains; t_v^* 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 t_m^* is also the characteristic time of the own, *i. e.* without the action *g*, rotation of *m*–ball [17].

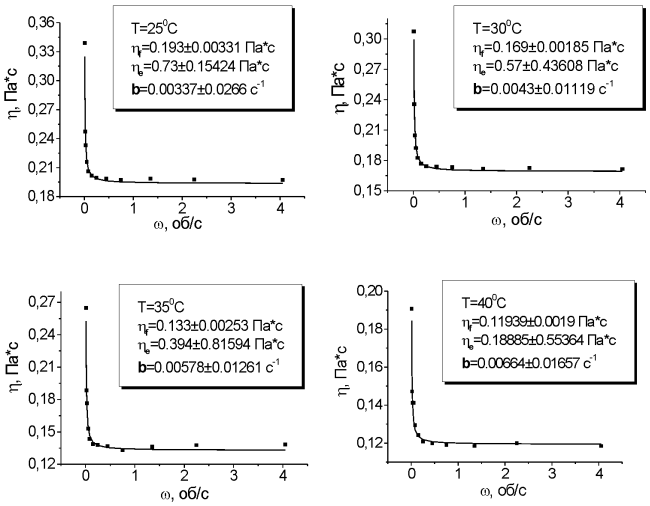

Fig. 1 – Experimental (points) and calculated in accordance with the equation (5) (curves) dependencies of the effective viscosity on the rotation velocity of the working cylinder: ρ = 4.0·10^5 *g/m*^{3}, *M* = 4.1·10^4 *g/mole*, *T* = 25 ÷ 40 ^0C

The expression (5) leads to the two asymptotes:

$\eta = \eta_f + \eta_e$ at $b/\omega >> 1$

$\eta = \eta_f$ at $b/\omega << 1$

So, it is observed a general regularity of the effective viscosity dependence on the rotation velocity ω of the working cylinder for diluted, concentrated solutions and melts. Under condition, that $b/\omega >> 1$, that is at $\omega \to 0$, the effective viscosity is equal to a sum of the frictional and elastic components of the viscosity, and under condition $\omega \to \infty$ 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* η_f, η_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 η_f are easy determined upon a plateau on the curves $\eta(\omega)$ accordingly to the condition $b/\omega << 1$ (*see Figures* 1–3). However, the optimization method gave not always the correct values of η_e and *b*. There are two reasons for this. Firstly, in a field of the $\omega \to 0$ 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 η on ω to the weak one the parameters η_e and *b* are interflowed into a composition $\eta_e b$, *i. e.* they are by one parameter. Really, at the

condition $b/\omega << 1$ decomposing the exponents into (5) and limiting by two terms of the row $exp\left\{-\frac{b}{\omega}\right\} \approx 1-\frac{b}{\omega}$, we will obtained $\eta = \eta_f + \eta_e b/2$.

Due to the above–mentioned reasons the optimization method gives the values of η_e and b depending between themselves but doesn't giving the global minimum of the errors functional. That is why at the estimation of η_e 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 η_e.

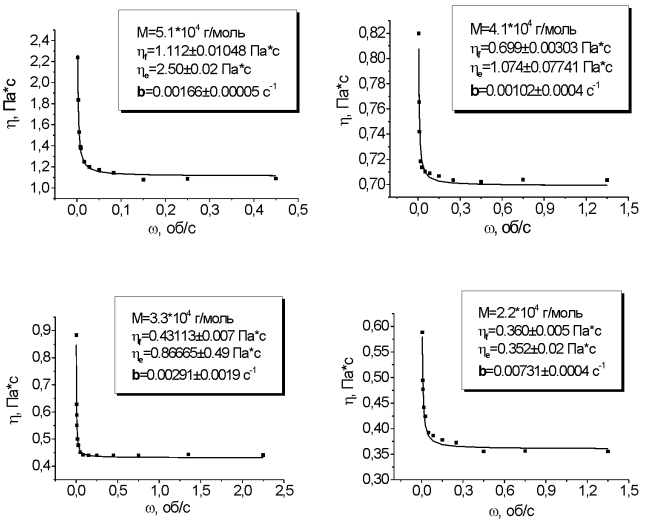

Fig. 2 - Experimental (points) and calculated in accordance with the equation (5) (curves) dependencies of the effective viscosity on the rotation velocity of the working cylinder: $\rho = 5.0\cdot10^5$ *g/m*^{3}, $M = 5.1 \div 2.2\cdot10^4$ *g/mole*, $T = 25\ ^0C$

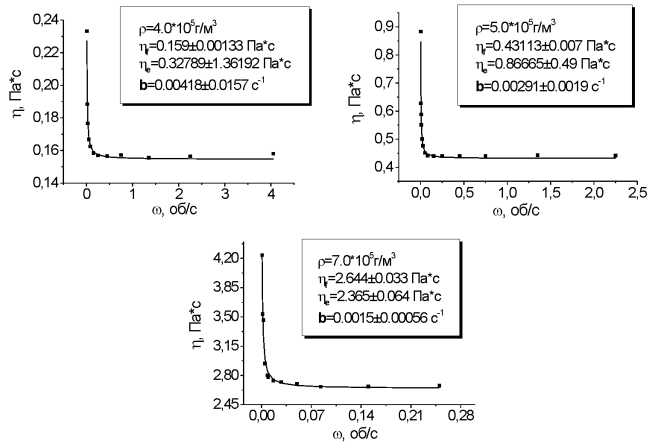

Fig. 3 - Experimental (points) and calculated in accordance with the equation (5) (curves) dependencies of the effective viscosity on the rotation velocity of the working cylinder: $\rho = 4.0\cdot10^5 \div 7.0\cdot10^5$ *g/m*^{3}, $M = 3.3\cdot10^4$ *g/mole*, $T = 25\ ^0C$

As we can see from the *Figures* 1–3, calculated curves *η(ω)* accordingly to the equation (5) and found in such a way parameters η_f, η_e and b, are described the experimental values very well.

The results of η_f, η_e and b numerical estimations for the all 48 experimental curves *η(ω)* are represented in *Table* 1. The mean–square standard deviations of the η_f, η_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 η_e and η_f are increased at the ρ 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:

$$\rho \geq \rho^*, \tag{7}$$

where ρ^* is a critical density of the solution per polymer corresponding to the starting of the polymeric chains conformational volumes overlapping having into diluted solution $\left(\rho \leq \rho^*\right)$ the conformation of *Flory* ball by the radius

$$R_f = aN^{3/5}, \tag{8}$$

here a is a length of the chain's link. It's followed from the determination of ρ^*

$$\rho^* = M / N_A R_f^3 = M_0 N / N_A R_f^3, \tag{9}$$

where M_0 is the molar weigh of the link of a chain. Taking into account the *eq. eq.* (8) and (9) we have:

$$\rho^* = \rho_0 N^{-4/5}, \tag{10}$$

where

$$\rho_0 = M_0 / a^3 N_A \tag{11}$$

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 ρ increasing. Moreover, not one, but m macromolecules with the same conformational radius are present into the conformational volume R_m^3. This leads to the notion of twisted polymeric chains m–ball for which the conformational volume R_m^3 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]:

$$R_m = R_f \cdot m^{1/5} \tag{12}$$

$$m^{1/5} = \left(\rho/\rho^*\right)^{1/2} \text{ at } \rho \geq \rho^*, \tag{13}$$

thus, it can be written

$$R_m = aN\left(\rho/\rho_0\right)^{1/2} \tag{14}$$

Table 1 - Optimization parameters η_f, η_e and b in equation (5)

$\rho\cdot10^{-5}$, g/m^3		4,0				5,0				7,0			
T, ^0C	$M\cdot10^4$ $g/mole$	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	η_f, $Pa\cdot s$	0,35	0,19	0,16	0,06	1,11	0,69	0,43	0,36	6,50	2,66	2,64	0,86
	η_e, $Pa\cdot s$	1,40	0,73	0,33	0,09	2,50	1,10	0,87	0,35	7,60	3,75	2,37	1,50
	$b\cdot10^3$, s^{-1}	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	η_f, $Pa\cdot s$	0,31	0,17	0,14	0,05	1,00	0,62	0,36	0,24	4,95	2,11	2,03	0,68
	η_e, $Pa\cdot s$	0,95	0,57	0,25	0,06	1,30	0,76	0,52	0,32	4,05	2,21	1,86	1,00
	$b\cdot10^3$, s^{-1}	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	η_f, $Pa\cdot s$	0,19	0,13	0,11	0,04	0,68	0,50	0,26	0,19	4,07	1,85	1,45	0,43
	η_e, $Pa\cdot s$	0,60	0,39	0,21	0,05	0,90	0,35	0,23	0,22	3,50	1,80	1,59	0,79
	$b\cdot10^3$, s^{-1}	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	η_f, $Pa\cdot s$	0,17	0,12	0,10	0,04	0,56	0,42	0,22	0,17	2,91	1,46	0,98	0,27
	η_e, $Pa\cdot s$	0,40	0,19	0,13	0,03	0,65	0,29	0,15	0,12	2,01	1,39	1,19	0,57
	$b\cdot10^3$, s^{-1}	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 μ for the *m*–ball was determined by the expression [19]:

$$\mu = 1.36\frac{RT}{N_A a^3}\left(\frac{\rho}{\rho_0}\right)^2 \qquad (15)$$

and, as it can be seen, doesn't depend on the length of a chain into the concentrated solutions.

Characteristic time t_m^* of the rotary movement of the *m*–ball and, respectively its shear, in accordance with the prior work [17] is equal to

$$t_m^* = \frac{4}{7}N^{3.4}\left(\frac{\rho}{\rho_0}\right)^{2.5} L_m\tau_m \qquad (16)$$

Let us compare the t_m^* with the characteristic time t_f^* of the rotary movement of *Flory* ball into diluted solution [17]:

$$t_f^* = \frac{4}{7}N^{1.4}L_f\tau_f\,. \qquad (17)$$

In these expressions τ_m and τ_f are characteristic times of the segmental movement of the polymeric chains and L_m and L_f 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 $\rho = \rho^*$ the expression (16) transforms into the *eq.* (17). The form factors L_m and L_f 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 η_f strongly depends on a length of the polymeric chains, on their concentration and on the temperature. The all spectrum of η_f dependence on *N*, ρ 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 η_s 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 η_{sm} 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 η_{pm} 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 η_f let us note via η_{pz}.

Not all the listed movement forms give the essential endowment into the η_f, 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:

$$\eta_f = \eta_s(1-\varphi) + (\eta_{sm} + \eta_{pm} + \eta_{pz})\varphi, \qquad (18)$$

or

$$\eta_f - \eta_s = (\eta_{sm} + \eta_{pm} + \eta_{pz} - \eta_s)\varphi, \qquad (19)$$

here φ 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:

$$\varphi = \bar{V}N / N_A R_m^3, \qquad (20)$$

in which $\bar{V}$ is the partial–molar volume of the monomeric link into solution.

Combining the *eq*. *eq*. (9)–(14) and *eq*. (20) we will obtain:

$$\varphi = \bar{V}\rho / M_0. \qquad (21)$$

The ratio of $M_0 / \bar{V}$ should be near to the density ρ_m of the liquid monomer. Assuming of this approximation, $M_0 / \bar{V} \approx \rho_m$ we have:

$$\varphi = \rho / \rho_m. \qquad (22)$$

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_m represents the averaged upon *m*–ball local velocity gradient of the hydrodynamic flow additional to *g*. Then, the tangential or strain shear σ formed by these gradients g_m and g at the rotation movement of *m*–ball in the medium of a solvent will be equal to:

$$\sigma = \eta_s(g + g_m). \qquad (23)$$

However, the measurable strain shear correlates with the well–known external gradient *g* that gives another effective viscosity coefficient:

$$\sigma = \eta_{pm} g \qquad (24)$$

Comparing the *eq*. (23) and eq. (24) we will obtain

$$\eta_{pm} - \eta_s = \eta_s g_m / g. \qquad (25)$$

Noting

$$\eta_{pm}^0 = \eta_s \cdot g_m / g \qquad (26)$$

instead of the *eq*. (19) we will write

$$\eta_f - \eta_s = (\eta_{sm} + \eta_{pm}^0 + \eta_{pz})\varphi \qquad (27)$$

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:

$$\eta_{pz} \sim \varphi^2. \qquad (28)$$

The efficiency of these contacts or linkages let us estimate comparing the characteristic times of the rotation (shear) of *m*–ball into concentrated solution t_m^* and polymeric ball into diluted solution t_f^* determined by the expressions (16) and (17).

Let's note that in accordance with the determination done by author [17] t_m^* is the characteristic time not only for *m*–ball rotation, but also for each polymeric chain in it. Consequently, t_m^* is the characteristic time of the rotation of polymeric chain twisted with others chains whereas t_f^* is the characteristic time of free polymeric chain rotation. The above–said permits to assume the ratio t_m^* / t_f^* as a measure of the polymeric chains contacts or linkages efficiency and to write the following in accordance with the (16) and (17):

$$\eta_{pz} \sim \mathrm{t}_\mathrm{m}^* / t_f^* = N^2 (\rho/\rho_0)^{2.5} (L_m / L_f) \qquad (29)$$

Taking into account the (22) and combining the (28) and (29) into one expression we will obtain:

$$\eta_{pz} = \eta_{pz}^0 N^2 \left(\frac{\rho}{\rho_0}\right)^{2.5} \left(\frac{\rho}{\rho_m}\right)^2 \qquad (30)$$

Here the coefficient of proportionality η_{pz}^0 includes the ratio $L_m \tau_m / L_f \tau_f$, which should considerably weaker depends on ρ and *N* that the value η_{pz}.

Substituting the (30) into (27) with taking into account the (22) we have:

$$\eta_f - \eta_s = \left[\eta_{sm} + \eta_{pm}^0 + \eta_{pz}^0 N^2 \left(\frac{\rho}{\rho_0}\right)^{2.5} \left(\frac{\rho}{\rho_m}\right)^2\right] \frac{\rho}{\rho_m} \qquad (31)$$

Let us estimate the endowment of the separate terms in *eq*. (31) into η_f. In accordance with *Table* 1 under conditions of our experiments the frictional component of the viscosity is changed from the minimal value ≈ $4 \cdot 10^{-2}$ *Pa·s* to the maximal one ≈ 6,5 *Pa·s*. Accordingly to the reference data the viscosity coefficient η_s of the toluene has the order $5 \cdot 10^{-4}$ *Pa·s*. The value of the viscosity coefficient η_{sm} representing the segmental movement of the polymeric chains estimated by us upon η_f of the diluted solution of polystyrene in toluene consists of the value by $5 \cdot 10^{-3}$ *Pa·s* order. Thus, it can be assumed η_{sm}, $\eta_s << \eta_f$ 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:

$$\eta_f \frac{\rho_m}{\rho} = \eta_{pm}^0 + \eta_{pz}^0 N^2 \left(\frac{\rho}{\rho_0}\right)^{2.5} \left(\frac{\rho}{\rho_m}\right)^2 . \qquad (32)$$

On *Fig.* 4 it is presented the interpretation of the experimental values of η_f into coordinates of the equation (32).

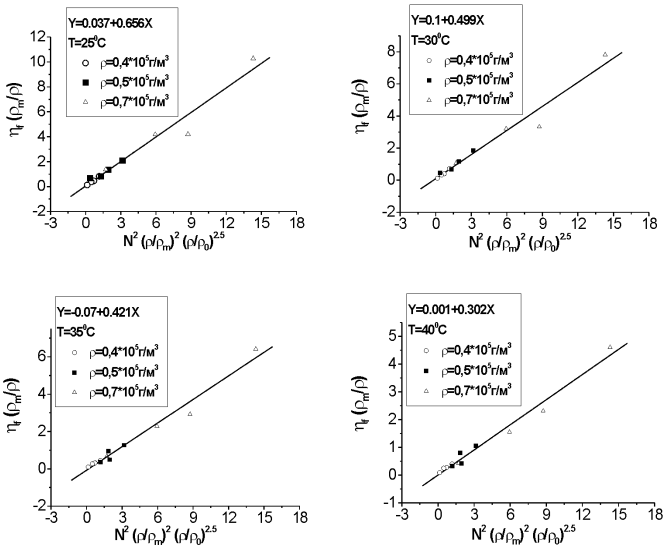

Fig. 4 - An interpretation of the experimental data of η_f in coordinates of the equation (32)

At that, it were assumed the following values: M = 104,15 *g/mole*, a = $1{,}86\cdot10^{-10}$ *m* under determination of ρ_0 accordingly to *eq.* (11) and $\rho_m = 0{,}906\cdot10^6$ *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 η_{pz}^0, the temperature dependence of which is shown on *Fig.* 5 into the *Arrhenius'* coordinates.

It is follows from these data, that the activation energy E_{pz} regarding to the movement of twisted polymeric chains in toluene is equal to 39,9 *kJ/mole*.

It can be seen from the *Fig.* 4 and from the represented regression equations on them, that the values η_{pm}^0 are so little (probably, $\eta_{pm}^0 << 0{,}1$ *Pa·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 g_m / g.

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 η_f on concentration of polymer into solution $\left(\eta_f \sim \rho^{5,5}\right)$ and on the length of a chain $\left(\eta_f \sim N^2\right)$.

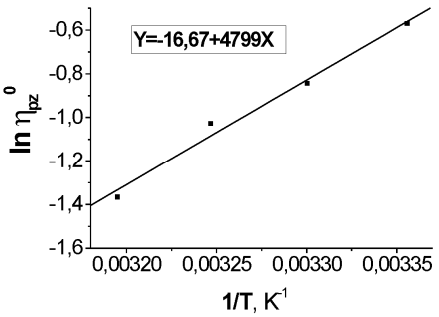

Fig. 5 - Temperature dependence of the viscosity coefficient η_{pz}^0 in coordinates of the *Arrhenius* equation

Elastic component of the effective viscosity

It is follows from the data of *Table* 1, that the elastic component of viscosity η_e is a strong increasing function on polymer concentration ρ, 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 μ, 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:

$$\eta_e = \mu t_m^* L_m . \qquad (33)$$

The factor of form L_m depends on the deformation degree of the conformational volume of a ball [17, 21].

Combining the (15) and (16) into (33) and assuming $\frac{4}{7}\cdot 1{,}36 \approx 1$ we will obtain

$$\eta_e = \frac{RT}{M_0} N^{3.4} \rho \left(\frac{\rho}{\rho_0}\right)^{3.5} L_m \tau_m . \qquad (34)$$

Comparing the (16) and (34) we can see, that the known from the reference data ratio $\eta_e \sim t_m^* \sim N^{3,4}$ is performed but only for the elastic component of a viscosity.

It is follows from the expression (34), that the parameters L_m and τ_m are inseparable; so, based on the experimental values of η_e (see *Table* 1) it can be found the numerical values only for the composition $L_m \cdot \tau_m$. The results of $(L_m \tau_m)\eta$ calculations are represented in *Table* 2. In spite of these numerical estimations scattering it is overlooked their clear dependence on T, but not on ρ and N.

Table 2 - Calculated values $L\tau$, τ/L, τ and L based on the experimental magnitudes η_e and b

$\rho\cdot10^{-5}$, g/m^3		4,0				5,0				7,0				$\tilde{\tau}\cdot10^{10}$, s
T, ^0C	$M\cdot10^4$, $g/mole$	5,1	4,1	3,3	2,2	5,1	4,1	3,3	2,2	5,1	4,1	3,3	2,2	$\tilde{L}$
25	$(L\tau)_{ne}\cdot10^{10}$, 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	
	$(\tau/L)_b\cdot10^{10}$, 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	
	$\tau\cdot10^{10}$, 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	$(L\tau)_{ne}\cdot10^{10}$, 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	
	$(\tau/L)_b\cdot10^{10}$, 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	
	$\tau\cdot10^{10}$, 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	$(L\tau)_{ne}\cdot10^{10}$, 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	
	$(\tau/L)_b\cdot10^{10}$, 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	
	$\tau\cdot10^{10}$, 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	$(L\tau)_{ne}\cdot10^{10}$, 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	
	$(\tau/L)_b\cdot10^{10}$, 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	
	$\tau\cdot10^{10}$, 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 t_v^* of g action on the shear strain of the *m*–ball and its rotation movement. Own characteristic time t_m^* of *m*–ball shear and rotation accordingly to (16) depends only on ρ, N and T via τ_m.

It is follows from the experimental data (see *Table* 1) that the *b* parameter is a function on the all three variables ρ, N and T, but, at that, is increased at T increasing and is decreased at ρ and N increasing. In order to describe these dependences let us previously determine the angular rate ω_m^0 (s^{-1}) of the strained *m*–ball rotation with the effective radius R_mL_m of the working cylinder by diameter d contracting with the surface:

$$\omega_m^0 = \pi d\omega / R_mL_m \qquad (35)$$

Here π is appeared due to the difference in the dimensionalities of ω_m^0 and ω.

Let us determine the t_v^0 as the reverse one ω_m^0:

$$t_v^0 = R_mL_m / \pi d\omega \qquad (36)$$

Accordingly to (36) t_v^0 is a time during which the *m*–ball with the effective radius R_mL_m 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 t_m^* 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 ω_m^0 was averaged out in accordance with the condition $d = (d_1 + d_2)/2$; so, respectively, the value t_v^0 was averaged out too:

$$t_v^0 = 2R_mL_m / \pi(d_1 + d_2)\omega. \qquad (37)$$

So, t_v^0 is in inverse proportion to ω; therefore through the constant device it is in inverse proportion to g: $t_v^0 \sim g^{-1}$. 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 g local averaged upon *m*–ball velocity gradient of the hydrodynamic flow g_m. This local gradient g_m 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 g_m into characteristic time t_v^* depends on the volumetric part φ of the links into the conformational volume of *m*–ball, *i. e.* $t_v^* \sim (g + g_m\varphi)^{-1}$.

Therefore, it can be written the following:

$$\frac{t_v^*}{t_v^0} = \frac{g}{g + g_m\varphi}, \qquad (38)$$

that with taking into account of *eq.* (37) leads to the expression

$$t_v^* = \frac{2R_mL_m}{\pi(d_1 + d_2)\omega} \Big/ \left(1 + \frac{g_m}{g}\frac{\rho}{\rho_m}\right). \qquad (39)$$

Combining the (16) and (39) into (6) we will obtain

$$b = \frac{7a}{2\pi(d_1 + d_2)} \cdot \frac{L_m}{\tau_m} \Big/ N^{2.4}\left(\frac{\rho}{\rho_0}\right)^2 \left(1 + \frac{g_m}{g}\frac{\rho}{\rho_m}\right). \qquad (40)$$

As we can see, here the parameters L_m and τ_m 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 $(\tau_m / L_m)_b$. After the substitution of values a = 1,86·10^{-10} *m*, d_1= 3,4·10^{-2} *m*, d_2= 3,3·10^{-2} *m* we have

$$\left(\frac{\tau_m}{L_m}\right)_b = 2.84\cdot 10^{-9} \Big/ N^{2.4}\left(\frac{\rho}{\rho_0}\right)^2\left(1+\frac{g_m}{g}\frac{\rho}{\rho_m}\right)b\cdot \qquad (41)$$

As it was marked, we could not estimate the numerical value of g_m / g due to the smallness of the value η^0_{pm} lying in the error limits of its measuring. That is why, we will be consider the ratio g_m / g 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, g_m / g was selected in such a manner that the factor of form L_m was near to the 1. This lead to the value g_m / g =25.

The calculations results of $(\tau_m / L_m)_b$ accordingly to equation (41) with the use of experimental values from *Table* 1 and also the values g_m / g =25 are represented in *Table* 2. They mean that the $(\tau_m / L_m)_b$ is a visible function on a temperature but not on a ρ and *N*.

On a basis of the independent estimations of $(\tau_m / L_m)_\eta$ and $(\tau_m / L_m)_b$ it was found the values of τ_m and L_m, 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 τ_m and *L* on *T*, but not on ρ and *N*. Especially clear temperature dependence is visualized for the values $\tilde{\tau}_m$, obtained via the averaging of τ_m at giving temperature for the all values of ρ and *N* (*Table* 2). The temperature dependence of $\tilde{\tau}_m$ into the coordinates of the *Arrhenius*' equation is presented on *Figure* 6.

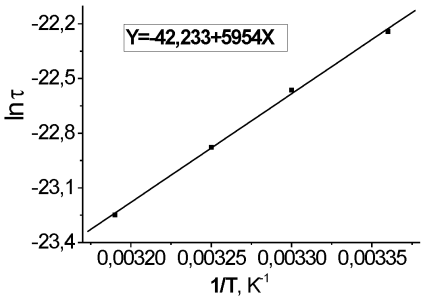

Fig. 6 - Temperature dependence of the average values of the characteristic time τ of the segmental movement of polymeric chain in coordinates of the *Arrhenius* equation

Conclusions

Investigations of a gradient dependence of the effective viscosity of concentrated solutions of polystyrene permitted to mark its frictional η_f and elastic η_e 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 t^*_m and Flory ball t^*_f. This lead to the dependence of the frictional component of viscosity in a form $\eta_f \sim N^2\rho^{5.5}$ 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 $\eta_e \sim N^{3.4}\rho^{4.5}$, that is lead to the well–known ratio $\eta_e \sim t^*_m \sim N^{3.4}$, which is true, however, only for the elastic component of the viscosity. On a basis of the experimental data of η_e and *b* it were obtained the numerical values of the characteristic time τ_m of the segmental motion of polymeric chains in concentrated solutions. As the results showed, τ_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 $\tilde{\tau}_m$.

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.

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© **Yu. G. Medvedevskikh** – сотр. отдела физической химии горючих ископаемых Института физико-органической химии и углехимии имени Л.М. Литвиненко Национальной академии наук Украины; **O. Yu. Khavunko** – сотр. отдела физической химии горючих ископаемых Института физико-органической химии и углехимии имени Л.М. Литвиненко Национальной академии наук Украины; **L. I. Bazylyak** – сотр. отдела физической химии горючих ископаемых Института физико-органической химии и углехимии имени Л.М. Литвиненко Национальной академии наук Украины; **G. E. Zaikov** –д.х.н., проф. каф. технологии пластических масс КНИТУ, ov_stoyanov@mail.ru.