ХИМИЯ, ТЕХНОЛОГИЯ И ИСПОЛЬЗОВАНИЕ ПОЛИМЕРОВ

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VISCOELASTIC PROPERTIES OF THE POLYSTYRENE IN CONCENTRATED SOLUTIONS AND MELTS (PART 2)

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 $\rho = 0{,}4\cdot10^5$; $0{,}5\cdot10^5$; $0{,}7\cdot10^5$ *g/m*^{3} *correspondingly for the fourth fractions of the polystyrene with the average molar weights* $M = 5{,}1\cdot10^4$; $4{,}1\cdot10^4$; $3{,}3\cdot10^4$; $2{,}2\cdot10^4$ *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 $\eta(\omega)$ 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 $\Delta S^*/R$ 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 $\rho = 0{,}4\cdot10^5$; $0{,}5\cdot10^5$; $0{,}7\cdot10^5$ г/м^3 соответственно для четырех фракций полистирола со средними молярными массами $M = 5{,}1\cdot10^4$; $4{,}1\cdot10^4$; $3{,}3\cdot10^4$; $2{,}2\cdot10^4$ 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 $\Delta S^*/R$ 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 $Pa\cdot s$) 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]:

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

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

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

in which the dimensionless function $f\left(gt^*\right) = f(x)$ 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 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 $M = 2{,}2\cdot10^4$ *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 $d_1 = 3{,}4\cdot10^{-2}$ and $d_2 = 3{,}9\cdot10^{-2}$ *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 $0{,}3^0$ angle and radius $r = 1{,}8\cdot10^{-2}$ *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 $\eta(\omega)$, the equation (5) [20] with the same remarks as to the numerical estimations of parameters η_e, η_f and b was used.

As it can be seen from the *Figures* 1 and 2, calculated curves of $\eta(\omega)$ accordingly to the equation (5) [20] with the founded parameters η_f, η_e and b describe the experimental data very well.

Results of the numerical estimations of η_f, η_e 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, η_e and η_f are increased at N increasing and are decreased at T increasing, whereas b parameter is changed into the opposite way.

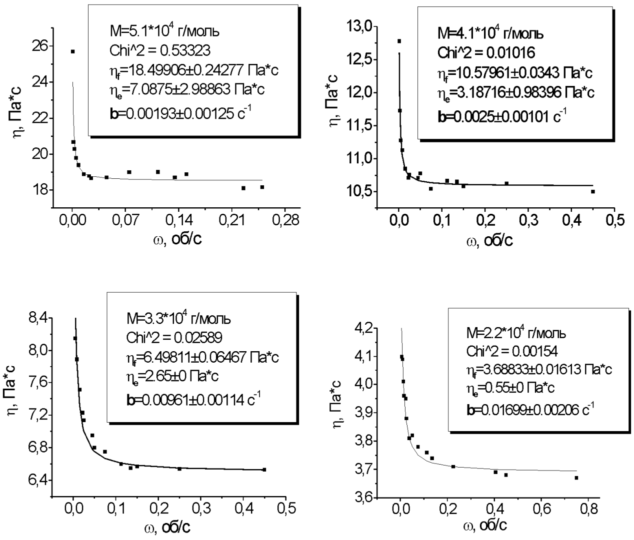

Fig. 1 - Experimental (points) and calculated in accordance with the equation (5) [20] (curves) dependencies of the effective viscosity on the velocity of the working cone rotation. T = 210 ^{0}C

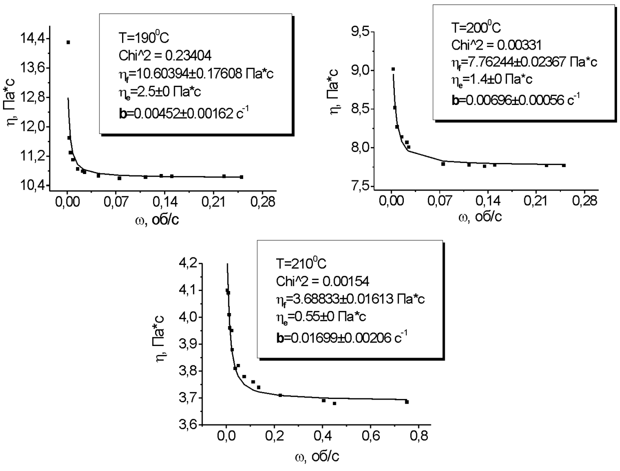

Fig. 2 - Experimental (points) and calculated in accordance with the equation (5) [20] (curves) dependencies of the effective viscosity on the velocity of the working cone rotation. *M* = $2{,}2\cdot10^4$ *g/mole*

Table 1 - Optimization parameters η_f, η_e and b obtained from the experimental data at T = 210 ^{0}C

$M \cdot 10^{-4}$, g/mole	η_f, Pa·s	η_e, 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 η_f, η_e and *b* obtained from the experimental data for polystyrene with $M = 2{,}2 \cdot 10^4$ *g/mole*

T, ^{0}C	η_f, Pa·s	η_e, 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 η_f very strongly depends on the length of the polymeric chains and on the temperature. The whole spectrum of the dependence of η_f 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 η_{sm}, η_{pm} and η_{pz} [20].

Not the all listed forms of the motion make the essential endowment into η_f, 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 $\eta_s = 0$, and $\varphi = 1$.

$$\eta_f = \eta_{sm} + \eta_{pm} + \eta_{pz} . \qquad (5)$$

In a case of the melts η_{pz} is determined by the equations (30) [20], but at $\varphi \cong \rho/\rho_m = 1$

$$\eta_{pz} = \eta_{pz}^0 N^2 \left(\frac{\rho}{\rho_0} \right)^{2.5} . \qquad (6)$$

Here the coefficient of the proportionality η_{pz}^0 contains the ratio L_m / L_f, however, since the melt is the ideal solution for polymer, that is why it can be assumed that $L_m = 1$.

By substituting of the (6) into (40) [20], we will obtain

$$\eta_f = \eta_{sm} + \eta_{pm} + \eta_{pz}^0 N^2 \left(\frac{\rho}{\rho_0} \right)^{2.5} \qquad (7)$$

Let's estimate an endowment of the separate components into η_f. 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 η_{sm}, which represents the segmental motion of the polymeric chains and estimated [21] on the basis of η_f for diluted solution of polystyrene in toluene is equal approximately $5 \cdot 10^{-3}$ *Pa·s*. Thus, it can be assumed that $\eta_{sm} << \eta_f$ and to neglect by respective component in (7). Taking into account of this fact, the expression (7) let's rewrite as follow:

$$\eta_f = \eta_{pm} + \eta_{pz}^0 N^2 \left(\frac{\rho}{\rho_0} \right)^{2.5} . \qquad (8)$$

For the melts $\rho/\rho_0 = const$, that is why the interpretation of the experimental values of η_f as the function of N^2 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 $\eta_{pz}^0 \left(\frac{\rho}{\rho_0} \right)^{2.5}$ 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 η_{pz}^0 it was assumed that $\rho = 1.05 \cdot 10^6$ *g/m*^{3}, ρ_0 was calculated in accordance with (11) [20] at M_0 = 104,15 *g/mole*, $a = 1{,}86 \cdot 10^{-10}$ *m*.

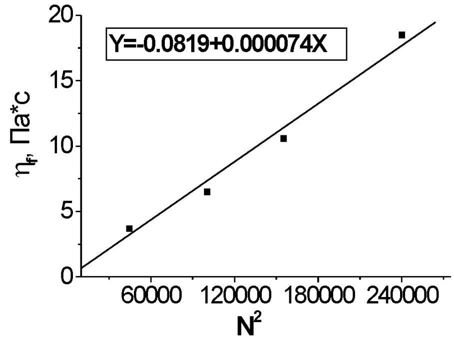

Fig. 3 - Interpretation of the experimental values of η_f in the coordinates of the equation (8) at T = 210 ^{0}C

Temperature dependence of η_{pz}^0 into coordinates of the Arrhenius equation is represented on Figure 4.

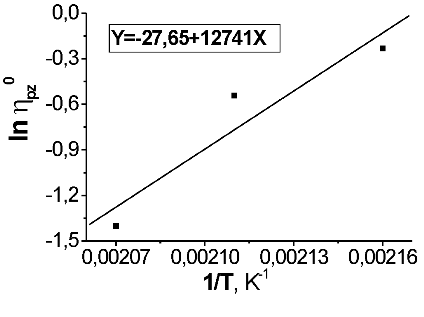

Fig. 4 - Temperature dependence of the numerical estimations of η_{pz}^0 in the coordinates of the Arrhenius equation

So, an activation energy $E_{pz,}$ 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 η_{pm}^{0} are very little and are within the ranges of their estimation error; this cannot give the possibility to estimate the value of g_m/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 η_f on the length of a chain ($\eta_f \sim N^2$).

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 η_e 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 $L_m = 1$.

$$\eta_e = \mu t_m^* \tag{9}$$

Correspondingly, instead of the (34) [20] we obtained

$$\eta_e = \frac{RT}{M_0} N^{3.4} \rho \left(\frac{\rho}{\rho_0}\right)^{3.5} \tau_m \tag{10}$$

Using the expression (10) and the experimental values of η_e (*see Table* 1 and *Table* 2) it was found the numerical values of the characteristic time of the segmental motion τ_m. The results of calculation $\left(\tau_m\right)_{\eta_e}$ 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 η_e and b ($M = 2.2 \cdot 10^4$ g/mole)

T, ^{0}C	$(\tau_m)_{\eta e} \cdot 10^{11}$, s	$(\tau_m)_b \cdot 10^{11}$, s	$\tau_m \cdot 10^{11}$, 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 η_e та b ($T = 210\ ^0$C)

$M \cdot 10^{-4}$, g/mole	$(\tau_m)_{\eta e} \cdot 10^{11}$, s	$(\tau_m)_b \cdot 10^{11}$, s	$\tau_m \cdot 10^{11}$, 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 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) [20] depends only on *N* and *T* via τ_m.

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 $\omega_m^0\ (s^{-1})$ of the rotation of m–ball with the effective radius R_m, which contacts with the surface of the working cone with radius *r*

$$\omega_m^0 = \pi r\omega / R_m \tag{11}$$

Here π is appeared as a result of the different units of the dimention $\omega_m^0, (s^{-1})$ and $\omega, (rot/s)$.

Let's determine the t_v^0 as the reverse one to the ω_m^0

$$t_v^0 = R_m / \pi r\omega \tag{12}$$

In equation (12) t_v^0 is a time during which the *m*–ball with the conformational radius R_m 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 t_m^* was determined by authors [17] also in calculation of the *m*–ball turning on the same single angle.

Thereby, t_v^0 is inversely proportional to ω, so via the constant of the device is inversely proportional to *g*: $t_v^0 \sim g^{-1}$. 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 g_m. This local gradient g_m 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 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.* $t_v^* \sim (g + g_m\varphi)^{-1}$. Into the melt $\varphi = 1$, therefore, it can be written the following:

$$t_v^* / t_v^0 = g / (g + g_m), \tag{13}$$

that leads with taking into account of the (12), to the expression

$$t_v^* = \frac{R_m}{\pi r\omega} \Bigg/ \left(1 + \frac{g_m}{g}\right). \tag{14}$$

By combining of the (16) [20] and (14) in (6) [20], we obtained

$$b = \frac{7a}{4\pi r \tau_m} \Bigg/ N^{2.4}\left(\frac{\rho}{\rho_0}\right)^2\left(1+\frac{g_m}{g}\right). \qquad (15)$$

As we can see, using the experimental values of *b* parameter (*see Table* 1 and *Table* 2) it can be calculated $\left(\tau_m\right)_b$. After the substitution of the values $a = 1.86 \cdot 10^{-10}$ *m*, $r = 1{,}8 \cdot 10^{-2}$ m, we obtained

$$\left(\tau_m\right)_b = 3.78 \cdot 10^{-6} \Big/ N^{2.4}\left(\frac{\rho}{\rho_0}\right)^2\left(1+\frac{g_m}{g}\right)b \cdot \qquad (16)$$

Numerical value of the ratio g_m/g was considered as a parameter, which selected in such a way, that calculated accordingly to (16) values of $\left(\tau_m\right)_b$ corresponded to the calculated values $\left(\tau_m\right)_{\eta_e}$ accordingly to (10). So, the obtained value of g_m/g = 39.

The results of calculations of $\left(\tau_m\right)_b$ and $\left(\tau_m\right)_{\eta_e}$, are compared in *Tables* 3 and 4. As the results show, $\left(\tau_m\right)_b$ and $\left(\tau_m\right)_{\eta_e}$ 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 $\widetilde{\tau}_m$ of the characteristic time of segmental motion of the macromolecule.

Temperature dependence of $\widetilde{\tau}_m$ into coordinates of the *Arrhenius* equation is represented on *Figure* 5.

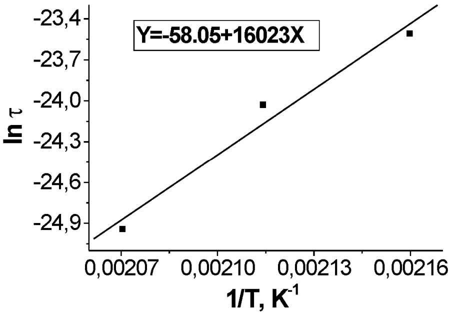

Fig. 5 - Temperature dependence of the averaged values of characteristic time τ of the segmental motion of polymeric chain into coordinates of the *Arrhenius* equation

Characteristic time of the segmental motion of polystyrene in solutions and melt

The presentation of values $\widetilde{\tau}_m$ into *Arrhenius*' coordinates equation (*Fig.* 6) [20] and (*Fig.* 5) permitted to obtain the expressions for concentrated solutions and melt, respectively:

$$\ln\widetilde{\tau}_m = -42.23 + 5950/T, \qquad (17)$$

$$\ln\widetilde{\tau}_m = -58.05 + 16020/T, \qquad (18)$$

For diluted solution of polystyrene in toluene it was early obtained [21]:

$$\ln\widetilde{\tau}_f = -44.07 + 6660/T, \qquad (19)$$

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]:

$$\tau = \frac{2h}{kT}\exp\left\{-\frac{\Delta S^*}{R}\right\}\exp\left\{\frac{\Delta H^*}{RT}\right\} = \tau_0 \exp\{E/RT\}, \qquad (20)$$

where $\Delta H^* = E$ is an activation energy of the segmental motion; ΔS^* 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 °*C* and for melt at *t* = 200 °*C* the values of the activation entropy $\Delta S^*/R$ = 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 ΔH_{evap} of styrene (–43,94 *kJ/mole*) and toluene (–37,99 *kJ/mole*). So, independently on fact, which values of ΔH_{evap} were taken for styrene or toluene, it is observed a general picture: $E_{\tau m}$, $E_{\tau f} > \Delta H_{вип}$. 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 °*C* 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 (t_t^*) and rotation (t_r^*) motions. As it was noted earlier, the characteristic time of the shear strain is also equal to t_r^*. 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 τ_s. 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 η_e 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 (η_{sm}), concentrated solution and melt (η_{pz}°).

The values τ_s will be used in the sequel for the estimation of the characteristic time of the translation motion t_t^* and of the coefficient of the diffusion *D* of the polystyrene chains into solutions and melt. Accordingly to the experimental data the temperature dependence τ_s, estimated based on the elastic component of the viscosity η_e and parameter *b*, is described by the equations:

in diluted solution (temperature range 20 – 35 º*C*)

$$\ln \tau_s = -44.07 + 6660/T, \qquad (21)$$

in concentrated solution (temperature range 25 – 40 º*C*)

$$\ln \tau_s = -42.23 + 5950/T, \qquad (22)$$

in melt (temperature range 190 – 210 º*C*)

$$\ln \tau_s = -58.05 + 16020/T \qquad (23)$$

Let's write also the temperature dependencies of the coefficients of a frictional component of the viscosity:

in diluted solution

$$\ln \eta_{sm} = -29.04 + 7300/T, \qquad (24)$$

in concentrated solution

$$\ln \eta_{pz}^{\circ} = -16.67 + 4800/T, \qquad (25)$$

in melt

$$\ln \eta_{pz}^{\circ} = -27.65 + 12740/T. \qquad (26)$$

Next, let's use the proposed earlier expression for characteristic time of the segmental motion in the following form

$$\ln \tau_s = \ln 2\frac{h}{kT} - \frac{\Delta S_s}{R} + \frac{E_s}{RT}, \qquad (27)$$

where $\ln 2\frac{h}{kT} =$ –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 $\Delta S_s/R$, which represented in *Table* 5.

In *Table* 5 also the activation energies E_s of the segmental motion and the value τ_s at *T* = 303 *K* and *T* = 473 *K* are represented too. Values τ_s 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	E_s, kJ/mole	$\frac{\Delta S_s}{R}$	E_{pz}, kJ/mole	$\frac{\Delta S}{R}$	T = 303 K		T = 473 K	
					τ_s, s	τ_{pz}, s	τ_s, s	τ_{pz}, s
Diluted solutions	55,3	15,3	—	—	$2{,}5\times 10^{-10}$	—	—	—
Concentrated solutions	49,4	13,5	39,9	6,0	$1{,}5\times 10^{-10}$	$6{,}0\times 10^{-9}$	—	$1{,}9\times 10^{-11}$
Melt	133,1	28,8	105,9	17,0	$5{,}6\times 10^{-3*}$	$1{,}5\times 10^{-2*}$	$3{,}1\times 10^{-11}$	$4{,}0\times 10^{-9}$

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 τ_s, and the thermodynamic characteristics ($\Delta S_s/R$ and E_s) 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 $\Delta S_s/R \approx 29$); as a result, the values of τ_s 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:

$$\eta_{sm} = 3\frac{RT}{V}\tau_{sm}, \qquad (28)$$

$$\eta_{pz}^{\circ} = 3\frac{RT}{V}\tau_{pz}, \qquad (29)$$

where *V* is the partial–molar volume of the monomeric link of a chain.

τ_{sm} and τ_{pz} 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:

$$V = \rho / M_0 \, , \tag{30}$$

where $\rho = 1.05 \cdot 10^6$ *g/m*^{3} is a density of the polystyrene melt; M_0 = 104.15 *g/mole* is the molar mass of styrene. Let us write (28) and (29) in general form:

$$\ln \eta = \ln 3RT \frac{\rho}{M_0} + \ln \tau \, \cdot \tag{31}$$

At this $\ln 3RT \frac{\rho}{M_0} = 18{,}15$ 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 τ_{sm} and τ_{pz} :

for diluted solution

$$\ln \tau_{sm} = -47.15 + 7300/T \, , \tag{32}$$

for concentrated solution

$$\ln \tau_{pz} = -34.82 + 4800/T \, , \tag{33}$$

for melt

$$\ln \tau_{pz} = -46.24 + 12740/T \, . \tag{34}$$

On the basis of two last ones expressions the τ_{pz} 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 $\Delta S_{pz}/R$ (see Table 5).

Comparing the parameters of the equation (21) for τ_s and (32) for τ_{sm}, it can be seen, that the difference between them is adequately kept within the error limits of their estimation. The values of τ_s and τ_{sm} at T = 303 *K*, equal to $2.5 \cdot 10^{-10}$ *s* and $1.0 \cdot 10^{-10}$ *s* correspondingly prove of this fact. Thus, it can be assumed that $\tau_s \equiv \tau_{sm}$, and that is why the coefficient of the frictional component of the viscosity η_{sm} 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 τ_{pz} 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 τ_s: $\tau_{pz} > \tau_s$, approximately on two orders. An analysis of the parameters of the equations (22), (23) and (33), (34) showed that the difference between τ_s and τ_{pz} is caused by two factors, which abhorrent the one of the other: by insignificant decreasing of the activation energy ($E_{pz} < E_s$), that should be decreased the τ_{pz}, and by a sharp decreasing of the activation entropy $(\Delta S_{pz} < \Delta S_s)$, that increases of τ_{pz}.

As it was said, the coefficient of the frictional component of viscosity η_{pz} 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 τ_s and τ_{pz} 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 ΔG_z° 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 $\exp\{-\Delta G_z^\circ / RT\}$. That is why, if the k_s is a constant rate of the free segmental transfer, and k_{pz} is the rate constant of the frozen segmental transfer, then between themselves the relationship should be existing:

$$k_{pz} = k_s \exp\{-\Delta G_z^\circ / RT\} \, . \tag{35}$$

Then k_{pz}, additionally to k_s, has a free activation energy equal to the standard free defrosting energy of the frozen state.

Since $k_s = \tau_s^{-1}$, $k_{pz} = \tau_{pz}^{-1}$, we obtained

$$\tau_{pz} = \tau_s \exp\{\Delta G_z^\circ / RT\} \, . \tag{36}$$

By assigning

$$\Delta G_z^\circ = \Delta H_z^\circ - T\Delta S_z^\circ \tag{37}$$

and taking into account the experimentally determined ratios $\tau_{pz} > \tau_s$, $E_{pz} < E_s$ and $\Delta S_{pz} < \Delta S_s$, we conclude, that in (37) $\Delta G_z^\circ > 0$, $\Delta H_z^\circ < 0$ and $\Delta S_z^\circ < 0$, and besides the entropy factor $T\Delta S_z^\circ$ should be more upon the absolute value than the enthalpy factor ΔH_z°. These ratios per the physical sense are sufficiently probable. A contact of the links under the gearing can activates a weak exothermal effect $(\Delta H_z^\circ < 0)$ 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 $\Delta S_z^\circ < 0$, but at this $\left|T\Delta S_z^\circ\right| > \left|\Delta H_z^\circ\right|$. Let's rewrite the (36) with taking into account of (37) in a form

$$\ln \tau_{pz} = \ln \tau_s + \frac{\Delta H_z^\circ}{RT} - \frac{\Delta S_z^\circ}{R} \, . \tag{38}$$

Comparing the expressions (22) and (33), (23) and (35) and taking into account (38) we obtained:
for concentrated solution

$\Delta G_z^\circ = 9.0$ *kJ/mole*, $\Delta H_z^\circ = -9.6$ *kJ/mole*, $\Delta S_z^\circ / R = -7.4$,

for melt

$\Delta G_z^\circ = 15.0$ *kJ/mole*, $\Delta H_z^\circ = -31.4$ *kJ/mole*, $\Delta S_z^\circ / R = -11.8$.

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 η_e°, and determined based on this value characteristic time of the segmental motion is τ_s; at the same time, the gearings effect strongly influences on the frictional component of viscosity, on the basis of which the τ_{pz} 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 τ_s for the estimation of dynamical properties of the polystyrene chains that is their characteristic time of the translational movement t_t^* and coefficient of diffusion *D* into solutions and melt. Accordingly to [26], the values t_t^* and *D* are determined by the expressions:
in diluted solutions

$$t_t^* = N^{8/5}\tau_s, \tag{39}$$

$$D = \frac{a^2}{2\tau_s} N^{-3/5}. \tag{40}$$

in concentrated solutions and melt

$$t_t^* = N^{3.4}\left(\frac{\rho}{\rho_0}\right)^{2.5}\tau_s, \tag{41}$$

$$D = \frac{a^2}{2\tau_s}\Big/\left(\frac{\rho}{\rho_0}\right)^{2.5} N^{2.4}. \tag{42}$$

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 τ_s and translational t_t^* motions of the polystyrene and diffusion coefficients *D*. It was assumed for the calculations $a = 1.86 \cdot 10^{-10}$ m, $N = 10^3$ and $\rho = 0.5 \cdot 10^6$ g/m^3 for concentrated solution and melt correspondingly. As we can see, the characteristic time of the translational motion t_t^* 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 t_t^* 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} *m*^{2}*/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 $D = 7 \cdot 10^{-22}$ *m*^{2}*/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 $10^{-21} \div 10^{-22}$ m^2/s.

Table 6 - Dynamic characteristics of polystyrene in solutions and melt

System	T = 303 K			T = 473 K		
	τ_s, s	t_t^*, s	D, m^2/sc	τ_s, s	t_t^*, s	D, m^2/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 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 $\eta_f \sim N^2$ 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 $\eta_e \sim N^{3.4}$, 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 melt. 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 $\tilde{\tau}_m$. In a case of a melt the value of E and $\Delta S^*/R$ 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.

References

1. Ferry J. D. Viscoelastic Properties of Polymers */ J. D. Ferry – N.Y.: John Wiley and Sons,* 1980. – 641 p.
2. De Gennes P. G. Scaling Concepts in Polymer Physics */ P.G. de Gennes – Ithaca: Cornell Univ. Press*, 1979. – 300 p.
3. Tsvietkov V. N. The Structure of Macromolecules in Solutions */ V. N. Tsvietkov, V. E. Eskin, S. Ya. Frenkel – M.: «Nauka»,* 1964. – 700 p. *(in Russian)*
4. Malkin A. Ya. Rheology: Conceptions, Methods, Applications */ A. Ya. Malkin, A. I. Isayev – M.: «Proffesiya»*, 2010. – 560 p. *(in Russian)*
5. Grassley W. W. The Entanglement Concept in Polymer Rheology */ W. W. Grassley // Adv. Polym. Sci.* – 1974. – v. 16. – p. p. 1–8.
6. Eyring H. Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates */ H. Eyring // J. Chem. Phys.* – 1936. – v. 4. – p. p. 283–291.
7. Peterlin A. Gradient Dependence of the Intrinsic Viscosity of Linear Macromolecules */ A. Peterlin, M. Čopic // J. Appl. Phys.* – 1956. – v. 27. – p. p. 434–438.
8. Ikeda Ya. On the effective diffusion tensor of a segment in a chain molecule and its application to the non-newtonian viscosity of polymer solutions */ Ya. Ikeda // J. Phys. Soc. Japan.* – 1957. – v. 12. – p. p. 378–384.
9. Hoffman M. Strukturviskositat und Molekulare Struktur von Fadenmolekulen */ M. Hoffman, R. Rother // Macromol. Chem.* – 1964. – v. 80. – p. p. 95–111.
10. Leonov A. I. Theory of Tiksotropy */ A. I. Leonov, G. V. Vynogradov // Reports of the Academy of Sciences of USSR.* – 1964. – v. 155. – № 2. – p. p. 406–409.
11. Williams M. C. Concentrated Polymer Solutions: Part II. Dependence of Viscosity and Relaxation Time on Concentration and Molecular Weight */ M. C. Williams // A. I. Ch. E. Journal*. – 1967. – v. 13. – № 3 – p. p. 534–539.
12. Bueche F. Viscosity of Polymers in Concentrated Solution */ F. Bueche //* J. Chem. Phys. – 1956. – Vol. 25. – P. 599 - 605.
13. Edvards S. F. The Effect of Entanglements of Diffusion in a Polymer Melt */ S. F. Edwards*, *J. W. Grant // Journ. Phys.* – 1973. – v. 46. – p. p. 1169–1186.
14. De Gennes P. G. Reptation of a Polymer Chain in the Presence of Fixed Obstacles */ P. G de Gennes // J. Chem. Phys.* – 1971. – v. 55. – p. p. 572–579.
15. Medvedevskikh Yu. G. Gradient Dependence of the Viscosity for Polymeric Solutions and Melts */ Yu. G. Medvedevskikh, A. R. Kytsya, L. I. Bazylyak, G.E Zaikov // Conformation of Macromolecules. Thermodynamic and Kinetic Demonstrations – N. Y.: Nova Sci. Publishing*, 2007. – p. p. 145–157.
16. Medvedevskikh Yu. G. Phenomenological Coefficients of the Viscosity of Low–Molecular Simple Liquids and Solutions */ Medvedevskikh Yu. G., Khavunko O. Yu. // Collection Book: Shevchenko' Scientific Society Reports* – 2011 – v. 28 – p. p. 70 – 83 *(in Ukrainian)*.
17. Medvedevskikh Yu. G. Viscosity of Polymer Solutions and Melts */ Yu. G. Medvedevskikh // Conformation of Macromolecules Thermodynamic and Kinetic Demonstrations – N. Y.: Nova Sci. Publishing,* 2007. – p. p. 125–143.
18. Medvedevskikh Yu. G. Statistics of Linear Polymer Chains in the Self–Avoiding Walks Model */ Yu. G. Medvedevskikh // Condensed Matter Physics*. – 2001. – vol. 2. – № 26. – p. p. 209–218.
19. Medvedevskikh Yu. G. Conformation and Deformation of Linear Macromolecules in Dilute Ideal Solution in the Self–Avoiding Random Walks Statistics */ Yu. G. Medvedevskikh // Journ. Appl. Polym. Sci,* 2008. – v.109. – № 4.
20. Medvedevskikh Yu.G., Khavunko O.Yu., Bazylyak L.I., Zaikov G.E. Viscoelastic properties of the polystyrene in concentrated solutions and melts (Part 1). Vestnik Kazanskogo tekhnologicheskogo universiteta. – 2014. – T.17. – №1. – P.155-164.
21. Medvedevskikh Yu. Frictional and Elastic Components of the Viscosity of Polysterene–Toluene Diluted Solutions */ Yu. Medvedevskikh, O. Khavunko // Chemistry & Chemical Technology* – 2011 – v. 5 – № 3 – p. p. 291–302.
22. Medvedevskikh Yu. G. Conformation of Linear Macromolecules in the Real Diluted Solution */ Yu. G. Medvedevskikh., L. I. Bazylyak, A. R. Kytsya // Conformation of Macromolecules Thermodynamic and Kinetic Demonstrations – N. Y.: Nova Sci. Publishing*, 2007. – p. p. 35–53.
23. Kuhn H. Effects of Hampered Draining of Solvent on the Translatory and Rotatory Motion of Statistically Coiled Long–Chain Molecules in Solution. Part II. Rotatory Motion, Viscosity, and Flow Birefringence */ H. Kuhn, W. Kuhn // J. Polymer. Sci.* – 1952. – v. 9. – p. p. 1–33.
24. Tobolsky A. V. Viscoelastic Properties of Monodisperse Polystyrene */ A. V. Tobolsky, J. J. Aklonis, G. Akovali // J. Chem. Phys.* – 1965. – v. 42. – № 2 – p. p. 723–728.
25. Medvedevskikh Yu. G. Kinetics of Bimolecular Radicals Decay in Different Polymeric Matrixes */ Yu. G. Medvedevskikh, A. R. Kytsya, O. S. Holdak, G. I. Khovanets, L. I. Bazylyak, G. E. Zaikov // Conformation of Macromolecules Thermodynamic and Kinetic*

Demonstrations – N. Y.: Nova Sci. Publishing, 2007. – p. p. 139–209.

26. Medvedevskikh Yu. G. Diffusion Coefficient of Macromolecules into Solutions and Melts / *Yu. G. Medvedevskikh // Conformation of Macromolecules. Thermodynamic and Kinetic Demonstrations – N. Y.: Nova Sci. Publishing*, 2007 – p. p. 107–123.

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