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KINETIC PARAMETERS OF SEGMENTAL AND TRANSLATIONAL POLYSTYRENE MOTION IN SOLUTIONS

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Abstract. An analysis of the characteristic times of the polystyrene segmental motion estimated on the basis of the elastic and frictional viscosity components of the polystyrenes solutions has been done. The characteristic times of the translational motion and also the diffusion coefficients of polystyrene in diluted and concentrated solutions were calculated.

Keywords: solution viscosity, characteristic time, segmental motion, coefficient of diffusion.

1. Introduction

Kinetics of the chemical processes proceeding with the formation of polymers (*namely*, polymerization, polycondensation) or with their participation (polymeranalogical transformations) in the most cases actually depends on the dynamic properties of the polymeric chains, *that is* on the characteristic times of their translational motion (t_t^*) and the rotary motion (t_r^*). Since the monomeric links connected into a chain, all of these types of the motions are realized purely in accordance with the reputation mechanism, *i. e. via* the segmental motion with the characteristic time τ_s.

2. Experimental

In order to obtain the statistically important experimental data, the gradient dependence of the viscosity for the diluted and concentration solutions of the polystyrene in toluene was studied [1, 2]. The experiments have been carried out with the use of the rotary viscometer "Rheotest 2.1" by VEB MLW production with the working cylinder containing two rotation surfaces.

The effective viscosity of polymeric solution was experimentally measured as the function of the angular rate ω (rps) of the working cylinder. The obtained results and the optimization method (Origin 5.0 program) were used for the determination of frictional η_f and elastic η_e components of the viscosity and also for b parameter [1, 2].

3. Results and Discussion

The characteristic times of the segmental motion τ were obtained on the basis of the experimental values of η_e and b. That is why let's analyze and generalize the obtained experimental data [1, 2] of the characteristic times of the segmental motion τ_s of the chains of polystyrene into solutions, estimated on the basis of the elastic component of the viscosity η_e. Besides, it is also necessary to take into account the characteristic times of the segmental motion, estimated on the basis of the frictional component coefficient of the viscosity of diluted (h_{sm}) [1] and concentrated (h_{pz}°) [2] solutions. Next, the values t_s will be used for the estimation of the characteristic time of the translational motion t_t^* and the diffusion coefficient D of the polystyrene chains in solutions.

Accordingly to the experimental data [1, 2] the temperature dependence t_s, estimated on the basis of the elastic component of the viscosity h_e, is described by the equations:

in diluted solution (temperature range 293–308 K)
$$\ln t_s = -44.07 + 6660/T \qquad (1)$$

in concentrated solution (temperature range 298–313 K):
$$\ln t_s = -42.23 + 5950/T \qquad (2)$$

Let us also write the temperature dependencies of the viscosity frictional component coefficients:

in diluted solution
$$\ln h_{sm} = -29.04 + 7300/T \qquad (3)$$

in concentrated solution

$$\ln h_{pz}^{\mathbf{o}} = -16.67 + 4800/T \qquad (4)$$

Characteristic time of the segmental movement is described by the expression [3]:

$$\ln t_s = \ln 2 \frac{h}{kT} - \frac{\Delta S_s}{R} + \frac{E_s}{RT} \qquad (5)$$

where $\ln 2 \dfrac{h}{kT} =$ -28.78 at $T = 303$ K

With the use of these values and comparing (5) and (1), (2), we obtain the numerical estimations for the activation entropy of the segmental movement $\Delta S_s/R$ (see Table). The activation energies E_s of the segmental movement and the value t_s at $T = 303$ K are also represented in this Table. The illustrated results showed, that the numerical values both t_s, and the thermodynamic characteristics ($\Delta S_s/R$ and E_s) of the segmental motion in diluted and concentrated solutions differed only within the limits of the experimental error of their estimations. Let's assume, that the coefficients of the frictional component of the viscosity of polymeric chains are described by the same general expression [3] as the coefficients of the viscosity of low-molecular solution. Then, it can be written:

$$h_{sm} = 3\frac{RT}{V}t_{sm} \qquad (6)$$

$$h_{pz}^{\mathbf{o}} = 3\frac{RT}{V}t_{pz} \qquad (7)$$

where V is the partial−molar volume of a monomeric link of the chain; t_{sm} and t_{pz} by content, the characteristic times of the segmental motion of free polymeric chains in diluted solution and their overlapping in concentrated solution, correspondingly.

Since the partial-molar volume V of the monomeric link of the polystyrene is unknown, then it can be assumed to be equal to the molar volume of the monomeric link into the melt: $V = r/M_0$, where $r = 1.05 \cdot 10^6$ g/m^3 is a density of the polystyrene melt; $M_0 = 104.15$ g/mol is the molar mass of styrene. Let us write (6) and (7) in the general form:

$$\ln h = \ln 3RT \frac{r}{M_0} + \ln t \qquad (9)$$

At this case, $\ln 3RT \dfrac{r}{M_0} = 18.15$ at $T = 303$ K. Taking into account this value and comparing (9) and (3) and (4), we obtained the temperature dependences t_{sm} and t_{pz}:
for diluted solution

$$\ln t_{sm} = -47.15 + 7300/T \qquad (10)$$

for concentrated solution

$$\ln t_{pz} = -34.82 + 4800/T \qquad (11)$$

in accordance with which t_{pz} and t_{sm} have been calculated at T = 303 K. Taking into account general Eq. (5), the value of the activation entropy $\Delta S_{pz}/R$ (see Table) has been found too. Comparing the parameters of the Eq. (1) for t_s and Eq. (10) for t_{sm}, we can see, that the difference between them is adequately kept within the error limits of their estimation. The values t_s and t_{sm} at $T = 303$ K, equal to $2.5 \cdot 10^{-10}$ s and $1.0 \cdot 10^{-10}$ s, correspondingly, prove this fact. Thus, it can be assumed that $t_s \equiv t_{sm}$, and that is why the coefficient of the frictional component of the viscosity h_{sm} of the polymeric chains can be described by the same general expression (6) as for the coefficient of the low-molecular solution. The values t_{pz} calculated accordingly to the expression (11) for concentrated solution at $T = 303$ K (see Table), essentially differed from t_s: $t_{pz} > t_s$, approximately by two orders. The analysis of Eqs. (2) and (11) parameters showed that the difference between t_s and t_{pz} is caused by two factors, which deny each other: the first is an insignificant decreasing of the activation energy ($E_{pz} < E_s$) that should decrease t_{pz}, and the second one is a sharp decreasing of the activation entropy ($\Delta S_{pz} < \Delta S_s$) that increases t_{pz}.

The coefficient of the frictional component of viscosity h_{pz} in concentrated solutions is caused by the motion of the overlapping between themselves polymeric chains characterizes the efficiency of all possible gearings. However, the mechanism of this motion is also reputational that is realized *via* the segmental motion. Correspondingly, the same relationship should exist between the times t_s and t_{pz}. Let's assume the thermodynamical approach for the determination of this relationship as one among all possible.

Let us determine the notion "gearing" as the thermodynamical state of a monomeric link of the chain, at which its segmental movement is frozen. It means that under the relative motion of the overlapped between eacj other polymeric chains the reputational mechanism of the transfer takes place due to the segmental movement, but only under condition that the part of the monomeric links of a chain is frozen.

Let $\Delta G_z^{\mathbf{o}}$ is a standard free energy of the monomeric link transfer from the free state into the frozen one. Then the probability of the frozen states formation (or their part) should be proportional to the value $\exp\{-\Delta G_z^{\mathbf{o}}/RT\}$. That is why, if k_s is a constant rate of the free segmental transfer, and k_{pz} is the rate constant of the frozen segmental transfer, then the relationship between themselves should exist:

$$k_{pz} = k_s \exp\{-\Delta G_z^{\mathbf{o}}/RT\} . \qquad (12)$$

**Characteristic parameters of the segmental
and translational movements of the polystyrene into solutions**

System	E_s, kJ/mol	$\dfrac{\Delta S_s}{R}$	E_{pz}, kJ/mol	$\dfrac{\Delta S_{pz}}{R}$	$T = 303$ K			
					t_s, s	t_{pz}, s	t_t^*, s	D, m^2/s
Diluted solution	55.3	15.3	——	—	$2.0 \cdot 10^{-10}$	—	$1.3 \cdot 10^{-6}$	$1.4 \cdot 10^{-12}$
Concentrated solution	49.4	13.5	39.9	6.0	$2.0 \cdot 10^{-10}$	$6.0 \cdot 10^{-9}$	$2.9 \cdot 10^{-4}$	$1.0 \cdot 10^{-13}$

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

Since $k_s = t_s^{-1}$, $k_{pz} = t_{pz}^{-1}$, we obtained:

$$t_{pz} = t_s \exp\{\Delta G_z^{\mathbf{o}}/RT\}. \tag{13}$$

By assigning

$$\Delta G_z^{\mathbf{o}} = \Delta H_z^{\mathbf{o}} - T\Delta S_z^{\mathbf{o}}, \tag{14}$$

and taking into account the experimentally determined ratios $t_{pz} > t_s$, $E_{pz} < E_s$ and $\Delta S_{pz} < \Delta S_s$, we conclude, that in (14) $\Delta G_z^{\mathbf{o}} > 0$, $\Delta H_z^{\mathbf{o}} < 0$ and $\Delta S_z^{\mathbf{o}} < 0$, and besides the entropy factor $T\Delta S_z^{\mathbf{o}}$ should be more upon the absolute value than the enthalpy factor $\Delta H_z^{\mathbf{o}}$. These ratios, by the physical content, are sufficiently probable. A contact of the links under the gearing can activates a weak exothermal effect $(\Delta H_z^{\mathbf{o}} < 0)$ at the expense of the intermolecular forces of interaction; the frosting of the segmental motion activates a sharp decrease of the entropy of monomeric link $\Delta S_z^{\mathbf{o}} < 0$, but at this $\left|T\Delta S_z^{\mathbf{o}}\right| > \left|\Delta H_z^{\mathbf{o}}\right|$. Let us rewrite (13) with taking into account (14) in the form of:

$$\ln t_{pz} = \ln t_s + \frac{\Delta H_z^{\mathbf{o}}}{RT} - \frac{\Delta S_z^{\mathbf{o}}}{R} \tag{15}$$

Comparing the expressions (2) and (11) and taking into account (15) we obtained: $\Delta G_z^{\mathbf{o}} = 9.0\,\text{kJ/mol}$; $\Delta H_z^{\mathbf{o}} = -9.6\,\text{kJ/mol}$; $\Delta S_z^{\mathbf{o}}/R = -7.4$. Next, let's use the obtained numerical values of the characteristic times of the segmental movement t_s for the estimation of dynamical properties of the polystyrene chains: namely, their characteristic time of the translational movement t_t^* and diffusion coefficient D in solutions. Accordingly to [4], the values t_t^* and D are determined by the expressions:

in diluted solutions

$$t_t^* = N^{8/5} t_s$$

and

$$D = \frac{a^2}{2t_s} N^{-3/5}$$

in concentrated solutions

$$t_t^* = N^{3.4} \left(\frac{r}{r_0}\right)^{2.5} t_s$$

and

$$D = \frac{a^2}{2t_s} \Big/ \left(\frac{r}{r_0}\right)^{2.5} N^{2.4}$$

where a is the length of a link of the polymeric chain, and N is their number; ρ is the concentration of a polymer into solution, g/m^3.

It was assumed for the calculations $a = 1.86 \cdot 10^{-10}\,\text{m}$, $N = 10^3$ and $r = 0.5 \cdot 10^6\,\text{g/m}^3$ for concentrated solution (see Table). As we can see, the characteristic time of the translational motion t_t^* of the polystyrene chains is by 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 in solutions is by 2−3 orders less, than the coefficients of diffusion of low−molecular substances, which are characterized by the order 10^{-9} m^2/s.

4. Conclusions

Thus, the 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 motions, on the basis of which the coefficients of diffusion of polymeric chains in solutions can be calculated.

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ХАРАКТЕРИСТИЧНІ ПАРАМЕТРИ СЕГМЕНТАЛЬНОГО І ПОСТУПАЛЬНОГО РУХУ ПОЛІСТИРОЛУ В РОЗЧИНАХ

Анотація. *Проведений аналіз характеристичних часів сегментального руху полістирену, оцінених за пружною та фрикційною компонентами в'язкості його розчинів. Оцінені характеристичні часи поступального руху і коефіцієнти дифузії полістирену у розведеному та концентрованому розчинах.*

Ключові слова: *в'язкість розчинів, характеристичний час сегментального руху, коефіцієнти дифузії.*