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 (polymeranalogue 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 \( \tau_t \) and the rotary motion \( \tau_r \).

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 \( \tau_s \).

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 \( \omega \) (rps) of the working cylinder. The obtained results and the optimization method (Origin 5.0 program) were used for the determination of frictional \( \eta_f \) and elastic \( \eta_e \) components of the viscosity and also for \( b \) parameter [1, 2].

3. Results and Discussion

The characteristic times of the segmental motion \( \tau \) were obtained on the basis of the experimental values of \( \eta_e \) and \( b \). That is why let’s analyze and generalize the obtained experimental data [1, 2] of the characteristic times of the segmental motion \( \tau_s \) of the chains of polystyrene into solutions, estimated on the basis of the elastic component of the viscosity \( \eta_e \). 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 \( \eta_{sm} \) [1] and concentrated \( \eta_{sz} \) [2] solutions. Next, the values \( \tau_s \) will be used for the estimation of the characteristic time of the translational motion \( \tau_t \) and the diffusion coefficient \( D \) of the polystyrene chains in solutions.

Accordingly to the experimental data [1, 2] the temperature dependence \( \tau_s \) estimated on the basis of the elastic component of the viscosity \( \eta_e \), is described by the equations:

- in diluted solution (temperature range 293–308 K) \[
\ln \tau_s = -44.07 + 6660/T
\] (1)
- in concentrated solution (temperature range 298–313 K): \[
\ln \tau_s = -42.23 + 5950/T
\] (2)

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

- in diluted solution \[
\ln \eta_{sz} = -29.04 + 7300/T
\] (3)
in concentrated solution
\[ \ln \eta^o = -16.67 + 4800/T \]  \hspace{1cm} (4)

Characteristic time of the segmental movement is described by the expression [3]:
\[ \ln \tau = \ln 2 \frac{h}{kT} - \frac{\Delta S}{R} + \frac{E_s}{RT} \]  \hspace{1cm} (5)

where \( \ln 2 \frac{h}{kT} = -28.78 \) 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 \( \Delta S/R \) (see Table). The activation energies \( E_s \) of the segmental movement and the value \( \tau \) at \( T = 303 \) K are also represented in this Table. The illustrated results showed, that the numerical values both \( \tau \), and the thermodynamic characteristics \( \Delta S/R \) 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:
\[ \eta_m = 3\frac{RT}{V} \tau_m \]  \hspace{1cm} (6)
\[ \eta^o = 3\frac{RT}{V} \tau^o \]  \hspace{1cm} (7)

where \( V \) is the partial—molar volume of a monomeric link of the chain; \( \tau_m \) and \( \tau^o \) 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: \( V = \rho/M_0 \), where \( \rho = 1.05 \times 10^4 \) g/m³ 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:
\[ \ln \eta = \ln 3RT \frac{\rho}{M_0} + \ln \tau \]  \hspace{1cm} (9)

At this case, \( \ln 3RT \frac{\rho}{M_0} = 18.15 \) at \( T = 303 \) K. Taking into account this value and comparing (9) and (3) and (4), we obtained the temperature dependences \( \tau_m \) and \( \tau^o \):

for diluted solution
\[ \ln \tau_m = -47.15 + 7300/T \]  \hspace{1cm} (10)

for concentrated solution
\[ \ln \tau^o = -34.82 + 4800/T \]  \hspace{1cm} (11)

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

The coefficient of the frictional component of viscosity \( \eta_m \) 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 \( \tau \) and \( \tau^o \). 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 each 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 \( \Delta G^o_m \) 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 \( \exp(-\Delta G^o_m/RT) \). That is why, if \( k \) is a constant rate of the free segmental transfer, and \( k^o \) is the rate constant of the frozen segmental transfer, then the relationship between themselves should exist:
\[ k^o = k \exp(-\Delta G^o_m/RT) \]  \hspace{1cm} (12)
Characteristic parameters of the segmental and translational movements of the polystyrene into solutions

<table>
<thead>
<tr>
<th>System</th>
<th>( E_s ), kJ/mol</th>
<th>( \Delta S_s / R )</th>
<th>( E_{ps} ), kJ/mol</th>
<th>( \Delta S_{ps} / R )</th>
<th>( \tau_s ), s</th>
<th>( \tau_{ps} ), s</th>
<th>( t'_s ), s</th>
<th>( D ), m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diluted solution</td>
<td>55.3</td>
<td>15.3</td>
<td>—</td>
<td>—</td>
<td>2.0 \times 10^{-10}</td>
<td>—</td>
<td>1.3 \times 10^{-6}</td>
<td>1.4 \times 10^{-13}</td>
</tr>
<tr>
<td>Concentrated solution</td>
<td>49.4</td>
<td>13.5</td>
<td>39.9</td>
<td>6.0</td>
<td>2.0 \times 10^{-10}</td>
<td>6.0 \times 10^{-9}</td>
<td>2.9 \times 10^{-4}</td>
<td>1.0 \times 10^{-13}</td>
</tr>
</tbody>
</table>

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

Since \( k_s = \tau_s^{-1} \), \( k_{ps} = \tau_{ps}^{-1} \), we obtained:

\[
\tau_{ps} = \tau_s \exp\left(\frac{\Delta G^o_s}{RT}\right).
\]

By assigning

\[
\Delta G^o_s = \Delta H^o_s - T \Delta S^o_s,
\]

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

\[
\ln \tau_{ps} = \ln \tau_s + \frac{\Delta H^o_s}{RT} - \frac{\Delta S^o_s}{R}.
\]

Comparing the expressions (2) and (11) and taking into account (15) we obtained: \( \Delta G^o_s = 9.0 \text{ kJ/mol} \); \( \Delta H^o_s = -9.6 \text{ kJ/mol} \); \( \Delta S^o_s / R = -7.4 \). Next, let’s use the obtained numerical values of the characteristic times of the segmental movement \( \tau_s \) for the estimation of dynamical properties of the polystyrene chains: namely, their characteristic time of the translational movement \( t'_s \) and diffusion coefficient \( D \) in solutions. Accordingly to [4], the values \( t'_s \) and \( D \) are determined by the expressions:

in diluted solutions

\[
t'_s = N^{3/5} \tau_s
\]

and

\[
D = \frac{a^2}{2 \tau_s} N^{-3/5}
\]

in concentrated solutions

\[
t'_s = N^{1.4} \left( \frac{\rho}{\rho_0} \right)^{2.5} \tau_s
\]

and

\[
D = \frac{a^2}{2 \tau_s} \left( \frac{D}{\rho_0} \right)^{2.5} N^{2.4}
\]

where \( a \) is the length of a link of the polymeric chain, and \( N \) is their number; \( \rho \) is the concentration of a polymer into solution, g/m³.

It was assumed for the calculations \( a = 1.86 \times 10^{-10} m \), \( N = 10^3 \) and \( \rho = 0.5 \times 10^6 g/m^3 \) for concentrated solution (see Table). As we can see, the characteristic time of the translational motion \( t'_s \) 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 \( t'_s \) 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.

References

ХАРАКТЕРИСТИЧНІ ПАРАМЕТРИ СЕГМЕНТАЛЬНОГО І ПОСТУПАЛЬНОГО РУХУ ПОЛІСТИРОЛУ В РОЗЧИНАХ

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

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