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On the length of statistical segment in flows of polymers

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Abstract

This paper presents a simple statistical model for calculations of the flow segment for polymer melts. The comparison of calculations with available data for five polymers demonstrates the model consistency. The model calculations show that the length of flow segment is generally more than the length of the Kuhn segment, and for high molecular weight polymers, the length of the flow segment is considerably less than the length of polymer chain between molecular entanglements. Our calculations also allowed for indirect evaluation of activation energies for monomer fluids, which are poorly determined from experimental data. © 2002 Published by Elsevier Science Ltd.

Keywords: Flow segment; Kinetic liquid theory; Flow activation energy

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1. Introduction

Many macroscopic phenomena, such as viscous flows, chemical reactions and diffusion, are represented by elementary acts of transition of molecular-kinetic units from one, quasi-equilibrium position to another. Eyring [1], who extended his theory of absolute reaction rates to diffusion processes and liquid flows proposed long ago a unified approach to these phenomena. Frenkel [2] analyzed the basic propositions of the Eyring theory. He argued that due to the energy fluctuation, the elementary transition act starts with supply of excess in energy from environmental particles to a single one. This creates an 'activated' particle whose excess in energy ('activation' energy) allows the particle to overcome a potential barrier separated the particles, and move it from one quasi-equilibrium position to another one. Immediately after that, the particle returns the excess of energy back to the environmental particles. This elementary act of transition can be accomplished only if the activated particle has a free space (a 'hole') in its vicinity, which provides the particle with a new quasi-equilibrium position where the particle can move in. The latter requirement is associated with simultaneous alteration in the quasi-equilibrium position of several environmental particles. Thus, the elementary act of transition in Eyring theory is a highly cooperative process. By analogy with chemical reactions, the energy required to overcome the potential barrier in flow is called flow activation energy.

Eyring and coworkers [1,3,4] had extensively used the concept of free volume and holes in liquids. They considered it as a necessary condition for elementary acts of transition in viscous flow. It was also argued [3], that the activation energy in flows of low molecular weight fluids (where the flow unit is the molecule itself) is closely related to the energy of vaporization. The ratio of the vaporization energy to the flow activation energy of low molecular weight liquids was found to be close to 4.

Kauzmann and Eyring [4] studied the flow of long chain molecules for series of *n*-alkanes. Using an empirical procedure, they showed that the size of the molecular-kinetic flow units (flow segments) becomes less than the total length of the molecule, as the length of molecule increases. Thus for polymers, the flow can be considered as succession of elementary transition acts in which only some parts of long molecule, the flow segments, participate.

Experimentally found relationship between the viscous flow activation energy and chain length for homologous series of *n*-alkanes (PE) [4], polystyrenes (PS) [5], polybutadienes (PBD) [6] and polydimethylsiloxanes (PDMS) [7,8] resulted in the fact that with increasing length of the macromolecule the flow segment becomes an increasingly smaller fraction of the macromolecular size. For very long molecules of *n*-alkanes, a limiting value of the length of the flow segment was found [4], which consists of about 20–25 carbon atoms. The activation energy of

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viscous flow of hydrocarbons of the same molecular length is approximately equal to that for the long chain LDPE.

In the present work, a semi-empirical statistical model is developed which allows calculating the length of flow segment in flows of polymers. The approach contains one fitting parameter, which should be found from available in the literature experimental data on the dependence of flow activation energy on polymer chain length.

2. Statistical model

In accordance with the Eyring concept, we consider the flow of polymers with long chain molecules as successive elementary acts of transition of relatively small, connected parts of macromolecule, flow segments, which overcome potential barriers to make rotation motions, consistent with connectivity, from one quasi-equilibrium conformation to another. These transitions can be considered as statistically independent and affected by random fluctuations of activation energy of rotation motions. We assume that fluctuation energy exceeds the rotational hindrance potentials, however, keeping chain connectivity. The amount of connected monomer units, n, participating in acts of transition can substantially vary. It is reasonable to assume, that this amount is proportional to the random excess in energy, E_n, i.e.

$$E_n = E_1 n. \tag{1}$$

Here E_1 is the value of the activation energy corresponding to the low molecular weight ('monomer') liquid. This assumption has been considered in paper [3].

To accomplish the elementary act of transition the flow segment, along with supply in a sufficient energy, should also possess a free space (a 'hole') in the vicinity of the original conformation to which a new equilibrium position of the flow unit can move. If P_{E} is the probability of the accumulation of sufficient energy to overcome the potential barrier and P_{H} the probability of the formation of hole near the initial equilibrium position, then the total probability P of the elementary transfer act to happen is [9]:

$$P = P_{\mathrm{E}} P_{\mathrm{H}}. \tag{2}$$

Various simplifications of Eq. (2) have been extensively analyzed in the literature. Eyring [1,3] identified the probability P with P_{E}. Other authors [10,11] used the free volume concept and associated the probability P with P_{H}. To resolve this uncertainty, more specific formulation of theory is required that involves some additional assumptions.

Below, we propose simplistic, intuitive arguments, which will lead to a simple formula for the total transitional probability in Eq. (2). Since these arguments are not supported by a real theoretical derivation, only extensive comparison with available in the literature experimental data may justify this approach.

We consider a highly simplified scheme for the description of thermal fluctuations due to the rotational segmental mobility for an averaged macromolecule, represented as a set of connected 'elementary' rotating segments. Here the length of the elementary segment represents a minimal amount of connected monomer units, which can perform a small random rotation motions consistent with geometric constraints. It should be mentioned that these rotation motions might also include those related to the changes of valence angles between adjusted monomer units. Because of that, the length of the elementary segment, except for two terminal monomer units, can be approximately considered as equal to two. We assume that the holes needed for the acts of elementary transition are readily available near this macromolecule. This is because in real chain dynamics, whenever the transition of the flow segments belonging to one macromolecule occurs, it leaves a hole nearby. It means that in our simplified averaged model there should be a lot of temporary holes.

We now make the crucial assumption: a transition act which involves r connected elementary segments can be equally presented in energetic sense as a random event of mutual, statistically independent r elementary acts (virtual or factual) involving these elementary segments, that after accomplishing the elementary act, preserve the connectivity of both the chain and segment.

Using this assumption, the probability $P_R(r)$ of transition for r connected elementary segments out of the chain consisting of R elementary segments, is easily found as:

$$P_R(R) \approx C_R q^r. \tag{3}$$

Here q is the probability of the elementary transition act for one elementary segment and C_R is a normalizing constant, which takes into account the finite number R of elementary segments in the chain. Bearing in mind that the elementary segment consists of n_{e} monomer units, we now represent formula (3) in the form:

$$P(n,N) = \frac{\mathrm{e}^{-an}}{\sum_{n=1}^{N} \mathrm{e}^{-an}} = \mathrm{e}^{-an}\,\frac{1-\mathrm{e}^{-aN}}{\mathrm{e}^{a}-1}. \tag{4}$$

Here $P(n,N)$ is the distribution function searched for, i.e. the probability of elementary transition for a flow segment, consisting of n monomer units in a chain molecule with the degree of polymerization N. The parameters in formula (3) are related to those in Eq. (4) as: $q = \exp(-a/n_{\mathrm{e}})$; $r = n/n_{\mathrm{e}}$; $R = N/n_{\mathrm{e}}$. The distribution function (4) contains only one model parameter, the constant a, whose physical sense is clarified later.

Even if distribution (4) is justified theoretically, the value of n in formulae (1) and (4) should be, strictly speaking, no less than that the size of the elementary segment. However, it is still possible to use approximately formulae (1) and (4) even in the asymptotic limit of simple monomer liquid when $n \to 1$.

The value of the average length n_N of the flow segment at given degree of polymerization N calculated using the probability distribution function in Eq. (4) is:

$$n_N \equiv \langle n(N) \rangle = \frac{\sum_{n=1}^{N} n\,\mathrm{e}^{-an}}{\sum_{n=1}^{N} \mathrm{e}^{-an}} = \frac{1}{1-\mathrm{e}^{-a}} - \frac{N}{\mathrm{e}^{aN}-1}. \quad (5)$$

Hereafter the square brackets denote the statistical average over distribution (4).

As expected, the averaged length of the flow segment is equal to 1 for the monomers when $N = 1$. For very long polymer chains, when $N \gg 1$ (a is fixed), the average flow segment length n_N has the limiting value, n_p defined as:

$$n_\mathrm{p} = \lim_{N\to\infty} n_N = \frac{1}{1-\mathrm{e}^{-a}}. \quad (6)$$

Formula (6) demonstrates the physical sense of the fitting parameter a as related to the limiting length of the flow segment for very long chain molecules. To express the parameter a through the observable parameters, we consider the average dependence of flow activation energy E_N on the chain length N. This dependence is easily obtained from Eqs. (1) and (4) as:

$$E_N = \langle E_1 n(N) \rangle = E_1 n_N. \quad (7)$$

Here E_1 is flow activation energy of monomer fluid. It is more convenient, however, to use instead of E_N the limiting value of flow activation energy E_p for very long chain polymers,

$$E_\mathrm{p} = E_1 n_\mathrm{p} = \frac{E_1}{1-\mathrm{e}^{-a}}. \quad (8)$$

The values of E_p are readily available in the literature. Combination of Eqs. (8) and (5) yield:

$$E_N = E_\mathrm{p}\left(1 - N\frac{1-\mathrm{e}^{-a}}{\mathrm{e}^{Na}-1}\right). \quad (9)$$

Based on Eq. (8) one can conclude that

$$n_\mathrm{p} = E_\mathrm{p}/E_1. \quad (10)$$

The size n_p of the flow segment depends on rigidity of macromolecules, increasing with the increase in their rigidity. The chain rigidity parameter σ (sometimes it is referred to as chain flexibility or stiffness), can be calculated for linear polymers as [9]:

$$\sigma = \sqrt{\langle L_0^2 \rangle / \langle L_\mathrm{f}^2 \rangle}. \quad (11)$$

Here $\langle L_0^2 \rangle$ is the mean-square distance between the ends of the unperturbed macromolecule in a theta-solvent, $\langle L_\mathrm{f}^2 \rangle$ is the same for a freely joined chain with fixed valence angles.

Higher values of the parameter σ correspond to more rigid polymer chain. The range of the values of parameter σ for most polymers is $1.5 < \sigma < 2.5$. Several authors [9,12] empirically observed a linear correlation between viscous flow activation energy E_p and logarithm of chain rigidity parameter, $\log \sigma$. Therefore the increase in the average length of the flow segment n_p is expected for high molecular weight polymers, as chain rigidity σ increases. Since range of values of σ is relatively small, we propose a simplified, linear empirical dependence between the chain rigidity parameter σ and the length of the flow segment n_p.

$$n_\mathrm{p} = \alpha + \beta\sigma. \quad (12)$$

If relation (12) is confirmed experimentally, the values of numerical parameters α and β should be treated as universal constants independent of polymer type.

Two approaches for determining the length n_p of the flow segment from experimental data could be in principle used for high molecular weight polymers, based on the earlier statistical model:

(i) The use of Eq. (9) for curve-fitting the relationship between the flow activation energy E_N and the polymer chain length N in order to find the parameter a, and then calculate the value n_p using formula (6); or
(ii) Direct calculation with the use of Eq. (10) when the values of E_1 are known.

The problem with the use of the straightforward approach (ii) is that the values of E_1 are either unknown or poorly determined in experiments. It is mainly because the common temperature range for the viscous flow of low molecular weight compounds (with the standard reference temperature 25 °C) in many cases is much lower than the Arrhenius region of viscous flow for high molecular weight polymers. For several polymers, such as PE, PDMS and PBD, both the regions, however, coincide. In this regard, we calculated in this paper, except one case, the length n_p using the approach (i) and employed formula (10) for evaluations of E_1.

3. Results and discussions

The crucial test for the presented model is the very possibility to fit with one parameter a the data available in the literature for the dependence of activation energy E_N on polymer chain length N. Unfortunately except for five polymers, we could not find experimental data available in the literature. These five polymers are: polyethylene (PE) [4], PS [5], PBD [6], PDMS [7,8] and polypentenylene (PPe) [13].

Fig. 1 shows plots of flow activation energies of homological series of these polymers normalized by the activation energy of long chain polymer E_p, versus chain length for these materials. The symbols in Fig. 1 denote experimental data obtained in the papers for the above five

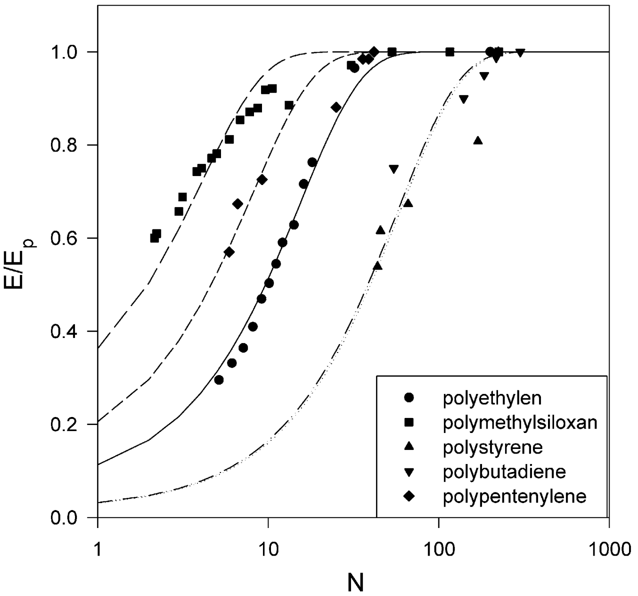

Fig. 1. Dependence of viscous flow activation energy on polymer chain length. Symbols are experimental results from references mentioned in text. Lines are results of calculation due to Eq. (9) with values of parameter a from Table 1.

polymers. The experiments in the cited references were performed in the temperature region in which polymer viscosity obeys Arrhenius equation, except for PS where the data presented were obtained at 175 °C (see discussion in Ref. [5]). Hence, the activation energies do not depend on temperature and typically were obtained as slopes of logarithmic plot of shear viscosity versus reciprocal temperature. More detailed descriptions of experimental methods are available in corresponding reference papers. Additionally, several studies demonstrated that variations in stereoregularity have little [6] or no [12] influence on flow activation energy. This is presumably because the activation energy is directly related to short-range interactions along the polymer chain, via steric hindrance and torque, which restrict internal rotations [12].

Lines in Fig. 1 present the least-square curve fitting of experimental data using formula (9). Thus obtained values of parameter a were used in formula (6) to yield the length of the flow segment n_p. Results of calculations along with other parameters used in discussions for the above five polymers, are presented in Table 1.

In an attempt to calculate the activation energy E_1 for monomer fluid when the data were not available, we tried to use an empirical relation [3] between the energy E_1 and the energy of vaporization,

$$E_1 \approx kE_{\mathrm{vap}}. \tag{13}$$

For ethylene, Kauzmann and Eyring [4] used the value $k = 1/4$. For other small molecules, the value of parameter k can be varied, depending on symmetry of molecular shape, e.g. for spherical molecules [3] such as CCl_4 and C_6H_6, etc. the value $k = 1/3$. We can assume that the more asymmetric is a molecule the less is the value of k. However, in our calculations of E_1, we used the value $k = 1/4$ since we cannot find more reliable data for highly elongated molecules such as pentene and butadiene. The values of E_1 for PS, PBD, and PPe calculated in such a way, are shown in Table 1, based on the values of E_{vap} provided in the text [14]. Data for E_1 in brackets presented in Table 1 were calculated using formula (10) and the values of n_p and E_p from Table 1. It is seen that the values of E_1 found for PS and PPe, using this procedure, highly disagree with those obtained with using the approach (i). It might be due to the fact that the value k used is higher than the actual one because of high asymmetricity of these molecules.

Using an additional empirical procedure, Kauzmann and Eyring [4] found that the flow segment of PE consists of 20–25 main chain carbon atoms. This is higher than our result. In the case of PDMS Wilcock [7] using similar procedure found flow segment to be consisting of 5–6 monomer units. It is closer to but less than our result ($n_p = 8.8$).

It should be noted that our calculation based on the experimental data [6] for PBD, a rather flexible polymer, resulted in a very high value of $n_p = 32$. It was especially surprising as we compared these results with these for the PPe, which is linear analog of 1,4-polybutadiene with an additional methylene group in its chain. In order to overcome this contradiction we assumed that the flow segment for both the polymers consists of the similar number of main chain molecular bonds. This assumption yields $n_p \approx 6$ for PBD. Additionally, in the case of PBD formula (10) should give

Table 1
The values of parameters for PE, PDMS, PS, PBD, and PPe used in calculations and discussions

Material	a	n_p	N_k Ref. [16]	N_e Ref. [17]	E_p (kJ/mol)	E_1 (kJ/mol)
PE	0.12	8.8	8	135	25	2.1 (2.84)
PDMS	0.45	2.8	9	140	16	7.2 (5.71)
PS	0.031	33	12	170	150	11.3^a (4.54)
PBD	0.032	6^b	–	60	34	5.8^a (5.67)
Ppe	0.23	4.9	–	–	19	6.3^a (3.88)

Data for E_p and E_1 are from reference papers for corresponding materials, unless otherwise noted. Data for E_1 in brackets were calculated using formula (10) and the values of n_p and E_p from Table 1.

[a] Calculated as $E_{\mathrm{vap}}/4$.

[b] The value was calculated using the method (ii).

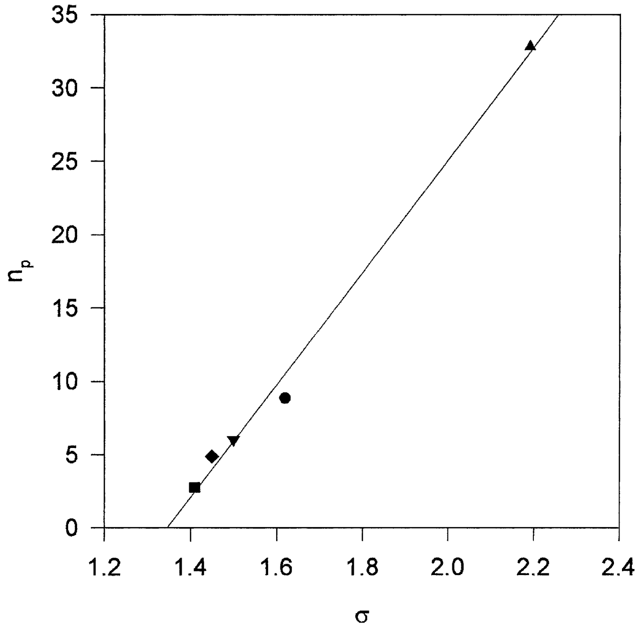

Fig. 2. Linear correlation between the average length of the flow segment n_p and the chain flexibility parameter. Symbols are as in Fig. 1. The line shows the result of linear regression.

reasonably accurate approximation for the value of E_1 since Arrhenius flow regions of polymer and monomer fluids coincide. As follows from Table 1, both calculations of E_1 for PBD are close to each other. Based on these arguments we believe that experimental data in paper [6] were not accurate. A possible explanation for the above discrepancy might be that the plot of E_N versus N for PBD in Ref. [6], provided the basis for calculations (i), was somewhat shifted toward the long molecular weight side. As the result, we consider the value of the flow segment length for PBD, $n_p = 6$, to be correct and will use it in the following discussion.

For our five polymers with higher molecular weight, the validity of the linear correlation given by Eq. (12) between chain rigidity parameter σ and the average length of the flow segment n_p is confirmed in Fig. 2. The values of numerical parameters α and β in Eq. (12) are found due to this figure as: $\alpha \approx -52$, $\beta \approx 38$. In Fig. 2, PDMS has the lowest value of n_p because silicon atoms add flexibility to the polymer chain [15]. PS with its very rigid chains, has the highest value n_p of all the polymers considered here. This is due to a big volume of the side group. Since the works [9,12] demonstrated the existence of a linear correlation between E_p and logarithm of chain rigidity parameter σ, the correlation in Fig. 2 gives also the possibility to evaluate independently the energy of activation E_1 for monomer fluids.

A brief comparison between the values of flow segment length n_p and available values of the Kuhn segment length, N_k [16], shown in Table 1, demonstrates that except for PDMS, the value of the Kuhn's segment length is as a rule less (and sometimes considerably) than the length of flow segment. The possible reason for the latter is unusual flexible Si–O–Si bond angle [15].

Finally, the comparison between the values of flow segment length, n_p, and values of length between molecular entanglements, N_e, (see, e.g. text [17]) shown in Table 1, demonstrates that $n_p \ll N_e$.

4. Conclusions

Based on molecular kinetic liquid theory and a simplified model approach, a statistical model was developed that can predict the length of the statistical flow segment for long chain molecules with one fitting parameter. Using this model and analysis of available literature experimental data, we determined the lengths of the flow segments for five narrow distributed polymers. For PE, PS, PB and PPe the following hierarchy among the length scale parameters holds: $N_k < n_p < N_e$. For PDMS, which is characterized by very flexible polymer chain we found that $N_k > n_p$. The numerical values of these parameters were summarized in Table 1. Since the activation energy in Arrhenius region cannot depend on temperature, it is clear from derivation that the length of flow segment is temperature independent. Our calculations also allowed for indirect evaluation of activation energies for monomer fluids, which are poorly determined from experimental data.

In addition, we found linear correlation between the values of chain flexibility parameter σ that can be readily determined from the geometry of molecular structure and length of the flow segment n_p. Based on this correlation, the length of the flow segment can be found for any narrow distributed polymer system.

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