

FREE VOLUME PARAMETERS OF POLY(DIMETHYLSILOXANE) FROM THE VISCOSITY MEASUREMENTS AT VERY LOW TEMPERATURES*

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The viscosity-temperature dependences for temperatures ranging from -65° to $+90^{\circ}\text{C}$ were measured for five poly(dimethylsiloxane) samples. For the same polymer the dependence of the Vogel parameters or of the free volume parameters on molecular weight was determined. The experimental range in the low-temperature region (non-constant flow activation energy), which was broader than in earlier papers, allowed more precise values to be obtained. The free volume parameters of poly(dimethylsiloxane), which had differed considerably from those of vinyl polymers, approached those of the latter group.

For the description of the dependence of viscosity of polymer melts on temperature in a region not too distant from the glass transition temperature, the empirical Vogel's equation¹

$$\eta = A \exp 1/\alpha(T - T_0) \quad (1)$$

or an analogous equation derived by Williams, Landel and Ferry² and made more exact by using the free volume theory³

$$\eta = A \exp (B/f) = A \exp \{B/[f_g + \alpha_f(T - T_g)]\} \quad (2)$$

proved to be useful.

The constant A depends only on the polymer structure. The parameters of Vogel's equation, α and T_0 , are said to be a function of molecular weight; however, no experimental dependence for any polymer has so far been published. The parameter f stands for the fractional free volume of the polymer, f_g is the same quantity at the glass transition reference temperature, α_f is the free volume expansion factor, T is the temperature of measurement and T_g is the glass transition temperature. The values given in the literature for the constant B vary from 0.57 to 1.67. According to the free volume theory it holds that $f_g/B = 0.025$; for a number of polymers the experimental value is very close to this figure.

For poly(dimethylsiloxane) both the parameter B and the fraction f_g/B are unusually high⁴. These data have been derived from the results of Plazek, Dannhauser and Ferry⁵ obtained by measuring one sample in the temperature range from -42.7

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to $+140.8^{\circ}\text{C}$. As the distance of experimental points from the glass transition temperature was rather large and the dependence $\log \eta$ vs $1/T$ was only very slightly curved within this range of temperatures, we regarded it as probable that the above dependence does not offer good conditions for treatment by using Eqs (1) and (2) and that the free volume parameters determined hencefrom may be subjected to a great error. We therefore decided to extend experimental measurements of poly(dimethylsiloxane) towards lower temperatures, to attempt a more reliable expression of the free volume parameters in this region and to examine their dependence on molecular weight.

EXPERIMENTAL

Polymers. Four of the five samples of poly(dimethylsiloxane) were silicone oils known under the trade name Lukooil (Synthesia, Kolín); the sample having the lowest molecular weight was prepared at the Research Institute of Organic Syntheses in Pardubice. Molecular weights were determined from the intrinsic viscosities of toluene solutions at 25°C by using the relationship⁶ $[\eta] = 8.28 \cdot 10^{-3} M_w^{0.72}$; the method of intrinsic viscosity measurements has been described in an earlier paper⁷. The results are summarized in Table I.

Viscometry. All measurements were carried out in capillary viscometers of the Ubbelohde type. The melt viscosity within the range of molecular weights used was independent of the velocity gradient. At temperatures from $+10^{\circ}$ to $+90^{\circ}\text{C}$ the samples were thermostated in an aqueous thermostat and the temperature was maintained with an accuracy of $\pm 0.05^{\circ}\text{C}$. In the region of lower temperatures the viscometers were immersed into a transparent Dewar flask filled with a mixture of ethanol with solid carbon dioxide having a temperature varying within $\pm 0.1^{\circ}\text{C}$. The measurements were conducted down to -65°C ; at lower temperatures with the exception of the sample having the lowest molecular weight the sample gradually solidified.

RESULTS

Parameters of Vogel's equation. The measured $\log \eta$ vs $1/T$ dependences are shown in Fig. 1. The curves plotted through experimental points have a slightly increasing slope; for the temperature region above 23°C the slope is virtually constant for all samples. The respective values of α and T_0 (Table I) were calculated with a Tesla 200 computer by employing a method suggested by Poďnecká and Quadrat⁸. The parameter T_0 somewhat increases with molecular weight; within the range of molecular weights used the difference between the T_0 values for the highest and lowest molecular weight is 15%. The values of the parameter α vary between $8.72 \cdot 10^{-4}$ and $9.40 \cdot 10^{-4}$, i.e. with a scatter of about 7%. The parameter α is closely connected with the flow activation energy E defined by

$$E = \partial \ln \eta / \partial (1/RT). \quad (3)$$

If viscosity is expressed by means of Eq. (1),

$$E = RT^2/\alpha(T - T_0)^2, \quad (4)$$

which for $T \gg T_0$ becomes

$$E = R/\alpha. \quad (5)$$

Hence it follows that both the parameter α and the flow activation energy E , if measured at $T \gg T_0$, must depend on molecular weight in the same way. Indeed, our data (for $M > 1.5 \cdot 10^3$) and the E values determined by Kataoka and Ueda⁹ (for $M > 2 \cdot 10^3$) are both independent of molecular weight.

Parameter B. By comparing Eqs (1) and (2) we express the constant B as the ratio of the free volume expansion coefficient α_f and the parameter α ,

$$B = \alpha_f/\alpha. \quad (6)$$

The expansion coefficient α_f is given by the difference between the expansion coefficient of the melt and that of the occupied volume

$$\alpha_f = \alpha_1 - \alpha_0. \quad (7)$$

α_0 can be regarded as the expansion coefficient α_g for crystal or for a solid polymer below T_g . According to Fox and Loshaek¹⁰, α_1 of poly(dimethylsiloxane) depends on the number average molecular weight obeying the relationship

$$\alpha_1 = 12 \cdot 10^{-4} + 1550 \cdot 10^{-4}/M_n. \quad (8)$$

We assume that our sample exhibits the most probable molecular weight distribution when $M_w/M_n = 2$ and that the viscosity average molecular weight M_η can be identi-

TABLE I
Free Volume Parameters of Poly(dimethylsiloxane)

Sample	M 7	M 50	M 100	M 200	M 350
M_η	1 500	5 700	10 400	15 800	21 900
$\alpha \cdot 10^4, K^{-1}$	9.40	8.81	8.79	8.72	9.19
T_0, K	60.0	61.2	66.8	66.0	67.8
B	1.21	1.04	1.01	1.00	9.99
$f(20^\circ C):$	0.253	0.216	0.206	0.204	0.201
f_g	-0.018	0.056	0.062	0.067	0.067

fied with the weight average M_w . This made it possible to calculate α_1 or after substitution of the tabulated value $\alpha_0 = \alpha_g = 3.2 \cdot 10^{-4}$ the free volume expansion coefficients corresponding to our samples; after substitution together with the average experimental value $\alpha = 9.0 \cdot 10^{-4}$ into (6) we calculated the dependence of the parameter B on molecular weight (Table I). B rapidly decreases with increasing molecular weight from 1.2 to a limit close to unity (Fig. 2).

The free volume fraction f . From Eqs (1), (2) the fractional free volume of a polymer can be written as

$$f = \alpha_f(T - T_0). \quad (9)$$

The results (Table I) are in very good accord with the values 0.24–0.18 obtained from the concentration dependence of viscosity by employing the method of Fujita and Kashimoto in our earlier paper⁷. In both cases the free volume fraction decreases with increasing molecular weight (Fig. 3).

The temperature term in Eq. (2) offers a possibility for determining the free volume at T_g from the known f , α_f and T_g . The glass transition temperature needed for this purpose was calculated from¹⁰

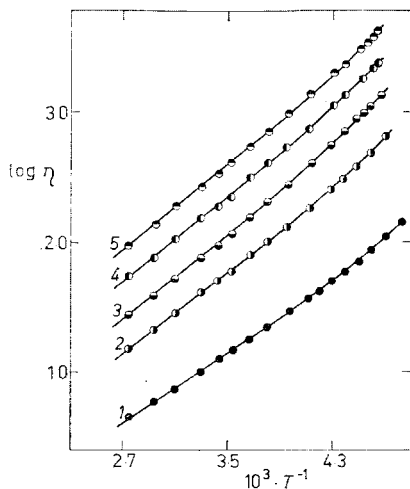


FIG. 1

Dependence of Viscosity η (cP) on Temperature T (K)

Polymer: 1 M 7, 2 M 50, 3 M 100, 4 M 200, 5 M 350.

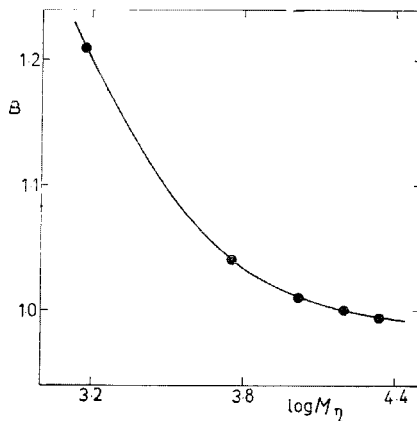


FIG. 2

Dependence of the Parameter B on Molecular Weight M_η

$$T_g = T_{g,\infty} - 0.8 \cdot 10^5 / M_n \quad (10)$$

(the tabulated¹¹ limiting T_g value for high molecular weights is $T_{g,\infty} = 123$ K). It can be seen (Table I) that the f_g values, with the exception of a sample having the lowest molecular weight, are independent of molecular weight. The average f_g/B value is a little more than twice 0.025, which is given in a review by Berry and Fox⁴ for polymers of the vinyl type. The nonreal negative f_g value for the sample M 7 and the slightly lowered value for the sample M 50 are a result of too low molecular weight for which Eq. (10) — which in actual fact is an extrapolation relationship of the T_g values in the vicinity of $T_{g,\infty}$ — is not suited.

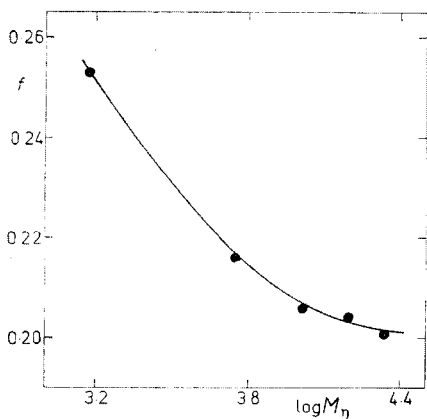


FIG. 3
Dependence of the Free Volume Fraction
on Molecular Weight M_n

DISCUSSION

Our extension of the experimental range towards lower temperatures leads to free volume parameters somewhat different from the data derived by Berry and Fox for poly(dimethylsiloxane) employing the data of Plazek and coworkers. The exceptional character of poly(dimethylsiloxane) has been greatly reduced and the results have approached the group of vinyl polymers. The parameter B has dropped from 1.67 to the theoretical value of unity, and f_g has dropped from 0.130 to 0.056–0.067. The reason should obviously be sought in a broader temperature range allowing a more precise expression of the constants of Vogel's equation. Since our lowest temperature used is higher by at least 85°C than T_g (which is still more than twice the value obtained for vinyl polymers), it is quite possible that no major difference could be found any more for the f_g or f_g/B values when interpreting experimental data from a region yet closer to T_g .

The constant B , as given by Berry and Fox⁴, could reflect the equilibrium flexibility of the main polymer chain, the size of substituents and their mobility; this however

has not yet been confirmed. We attempted to estimate this influence by using data for polyisobutylene, polystyrene, poly(vinyl acetate) and poly(methyl methacrylate) tabulated in the literature⁴, as well as our values for poly(dimethylsiloxane). The ratio s_0^2/Z , where $(s_0^2)^{1/2}$ is the radius of gyration of an unperturbed polymer coil and Z is the number of atoms in the backbone of the polymer chain, was taken as the measure of rigidity. This measure was found to be independent of the parameter B .

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