USE OF BUECHE'S FUNCTION IN THE ANALYSIS OF THE DEPENDENCE OF THE VISCOSITY OF POLYDIMETHYLSILOXANE ON MOLECULAR WEIGHT*

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A detailed analysis of the dependences of the viscosities of melts of various polymers on molecular weight published so far has revealed that the change in the slope at the so called critical molecular weight is continuous. This continuous dependence is best described by Bueche's function for the model of entangled chains, as follows from the analysis of experimental results taken from a paper by Kataoka and Ueda for the polydimethylsiloxane melt. The values of Bueche's function are tabulated.

Berry and Fox[1] have proved for a number of polymer melts that the experimental course of the dependence of viscosity on the weight average molecular weight in the logarithmic plot consists of two linear branches with slopes 1 and 3·4. They regard the change in the slope in the transition region as a consequence of an essential change in the structure of the melt when the polymer chains become entangled and the formation of entanglements sets in. The molecular weight corresponding to the break in slope on the dependences is called critical. A closer investigation of the plots after magnification showed that the change in the slope in the vicinity of the critical molecular weight is a continuous one. We believe that this finding is not at variance with the conception of entanglement formation in the melt: on the contrary, one can assume the existence of entanglements also at low molecular weights; the degree of entanglement formation and thus also the slope of the $\log \eta$ vs $\log M_w$ dependence will increase continuously with molecular weight.

The dependence of viscosity on the length of macromolecules for the model of entangled chains was theoretically derived by Bueche[2,3]. He obtained the expression

$$\eta = (N/6) \left(\overline{s_0^2}/M\right) Z \varrho \Gamma_1 \Gamma_2 \zeta, \qquad (1)$$

where

$$\Gamma_1 = 1 + 4K\lambda^{3/2} \sum_{n=1}^{\infty} s^n (2n - 1)^{3/2} \left[1 - \exp(-B_n)\right], \qquad (2)$$

$$B_n^{-1} = 4K(2n - 1)^{3/2} \lambda^{(3/2)-n}, \qquad (3)$$

and

$$\Gamma_2 = 1 + \lambda/4 ; \qquad (4)$$

N denotes Avogadro number, $(\overline{s_0^2})^{1/2}$ is the radius of gyration of an unperturbed polymer coil, M is molecular weight, Z is the number of atoms in the backbone of the polymer chain, ϱ is density, and ζ is the frictional factor corresponding to one link in the chain. For common systems the author gives — besides very low Z values — a constant K ranging from 1 to 3. For the parameter it holds $\lambda = Z/2Z_e$, where Z_e is the number of atoms in the chain between entanglement points. The factor s defines the strength of the entanglement couple; $s = 0$, if the couple results in no constraint on the molecular motion, and $s = 1$, if the couple acts as a permanent bond. Unfortunately, Bueche's equation does not allow direct calculation of viscosity as a function of molecular weight, because it contains unknown adjustable parameters s, Z_e and K. Nevertheless, Bueche[3] used the simplified relationship (2) for the limiting regions of low and high molecular weights to calculate the slopes 1 and 3·5 which were in satisfactory agreement with the experimental data.

Since Bueche's function describes the change in viscosity due to entanglement formation, the degree of which increases with increasing chain length or with the number of couple points in this chain, it seemed desirable to find out whether this function could also be applied to the interpretation of the continuous experimental dependence log η vs log M in the critical region of M. For the case of a similar theoretical and experimental course there arose the possibility of determination of the numerical values of the parameters s and Z_e. The viscosity described by (1) is proportional to the expression $\lambda\Gamma_1\Gamma_2$; the dependence log η vs M should therefore be compared with the dependence log $(\lambda\Gamma_1\Gamma_2)$ vs log λ. We wanted to investigate such range of λ which would allow the limiting regions for low and high molecular weights to be expressed in a sufficient width. However, it follows from the definition of the parameter λ that at $Z < Z_e$, *i.e.* at log $\lambda < -0.301$ this quantity loses its physical meaning. According to Bueche's theory, participation of all macromolecules in entanglement formation in the system is considered in this case. In our opinion it can be assumed that entanglement process occurs also if $Z < Z_e$, but with the participation of a still lower number of macromolecules, which can be described by Bueche's function with fictitious Z values lower than Z_e. Although the theoretical dependence log $\lambda\Gamma_1\Gamma_2$ vs log λ for $Z = Z_e$ was already an almost straight one with a unit slope, we extended the region of log λ under investigation from -1.4 to 2.0. A desk

programmed computer WANG 600 was used for the calculations; the results for the parameter s ranging from 0·1 to 0·3 which Bueche regarded as the most probable ones, and for the values of the parameter K ranging from 1 to 3, are given in Tables I—III. The effect of the parameter K on the dependence $\log(\lambda\Gamma_1\Gamma_2)$ vs $\log\lambda$ appeared to be practically negligible. It can be seen that the increase in the slope of Bueche's function in the transition region is continuous as in the experimental dependences of viscosity on molecular weight (Fig. 1). In order to find out to what extent these functions coincide quantitatively one had to analyze also the remaining terms in relationship (1), $i.e.$ the characteristic ratio $\overline{s_0^2}/M$, density and frictional factor, with respect to their possible dependence on molecular weight.

The frictional factor ζ is a function of temperature and depends on molecular weight only at its lower values. Consequently, the plot $\log\eta$ vs $\log M_w$ may be concave, as shown by Allen and Fox[4] for polystyrene, and the slope of the tangent to this plot is greater than unity. The course of the dependence of viscosity or of the frictional factor on temperature is related to the distance of the temperature used from the glass transition temperature T_g. At temperatures more distant from T_g the flow activation energy $E = \partial\ln\eta\,\partial(1/RT)$ is constant. Nearer to T_g it increases with decreasing temperature, and the dependence of the frictional factor on temperature in this region is very adequately described by Vogel's empirical equation[5]

$$\ln\xi = \ln\xi_0 + 1/\alpha(T - T_0),\qquad(5)$$

or by its modification[4]

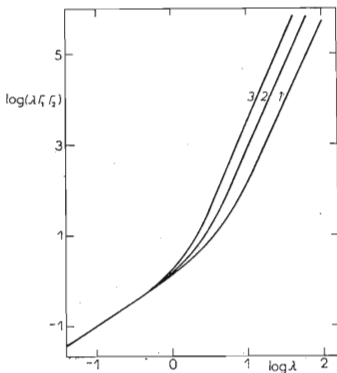$$\ln\xi = \ln\xi_{00} + W/T + 1/\alpha(T - T_0).\qquad(6)$$

FIG. 1

Bueche's Function $\log(\lambda\Gamma_1\Gamma_2)$ vs $\log\lambda$ for $K = 2$

s: 1 0·1, 2 0·2, 3 0·3.

The parameters α, T_0 and W should depend on molecular weight, the characteristic frictional factor ξ_{00} is allegedly independent of the molecular structure, and $\log \xi_{00} = = -10.6$ should be universal for all polymers[1].

The prevailing majority of the results of measurements of the temperature dependences of polymer melts given in the literature exhibits a nonconstant activation energy. The dependence of the parameters α, T_0 and W on molecular weight has not yet been investigated for any polymer at all. The exception to these systems is polydimethylsiloxane with constant flow activation energy already at room temperatures and higher. According to the measurements by Plazek, Dannhauser, and Ferry[6] carried out at the temperature interval between $-42.7°C$ and $140.8°C$, the dependence $\log \eta$ vs $1/T$ is practically linear starting from $-23°C$; for lower temperatures it is only slightly curved. The reason should obviously be sought in the exceptionally low glass transition temperature T_g 150 K.

With respect to the constant activation energy, the temperature dependence of the frictional coefficient for polydimethylsiloxane at 25°C can be described by a simple relationship

$$\ln \xi = \ln \xi_{00} + E/RT. \tag{7}$$

Since the experimental data of the dependence of the activation energy, density and viscosity of this polymer have been tabulated by several authors (Kataoka and
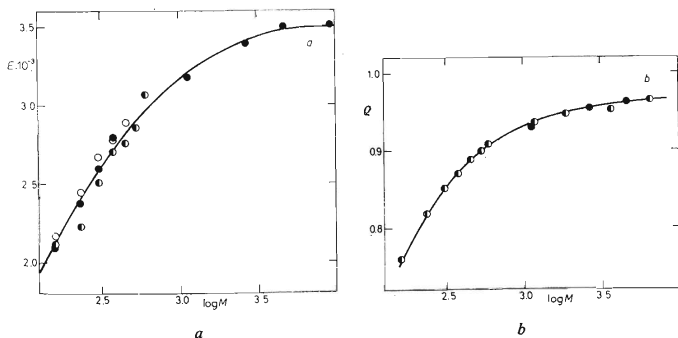
Fig. 2

Dependence of the Flow Activation Energy E [cal mol^{-1}] (a) and of Density ϱ (b) on Molecular Weight

○ Hurd[9], ◐ Hunter and coworkers[8], ● Kataoka and Ueda[7]; full line represents the dependence calculated (a) according to (8), (b) according to (9).

Ueda[7], Hunter[8], Hurd[9]), we used these data for a more detailed analysis of Bue-che's function.

The flow activation energy increases with increasing molecular weight[7-9] and reaches the limiting value of E_∞ $3.55 . 10^3$ cal/mol at approximately $M \simeq 15000$. We found that such experimental course can very well be approximated (Fig. 2a) by the empirical formula

$$E = E_\infty - B/(A + M). \tag{8}$$

The constants $A = 122$ and $B = 394 \times 10^3$ were determined by plotting the data tabulated in the papers referred to above[7-9] and from the intercept of the straight dependence $1/(E_\infty - E)$ vs M.

Similarly, an analogous dependence of density[7,9] (Fig. 2b) was described by

$$\varrho = \varrho_\infty - C/(D + M) \tag{9}$$

with the constants $\varrho_\infty = 0.970$, $C = 40$, and $D = 24$.

The decrease in the characteristic ratio $(\overline{s_0^2}/M)$ with molecular weight is small, and can there-fore be neglected. A constant value of $7.2 . 10^{-18}$ from the paper by Berry and Fox[1] was used in the calculations. The weight of a part of the polymer corresponding to one atom of the poly-dimethylsiloxane chain was taken as one half of the weight of the group $-Si(CH_3)_2O-$, i.e. $M_0 = 37$. Then we have $Z = M/M_0 = M/37$. (We are aware of the fact that at very low mole-cular weights the relationship between Z and M will be somewhat different owing to the effect of the endgroups; the problem remains how to define it in this region.)
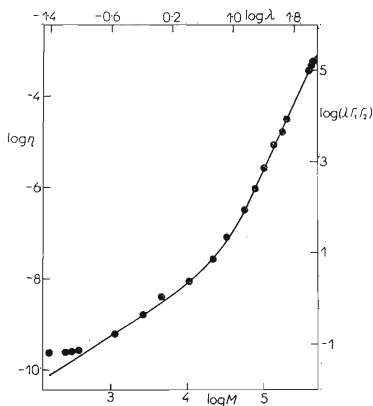

Fig. 3

Dependence of $\log \eta'$ on $\log M$ Calculated from (10) According to the Data Tabulated by Kataoka and Ueda[7]

Full line represents Bueche's function for $s = 0.1$.

By substituting the frictional factor expressed by (7) into Bueche's equation we can describe the characteristic frictional factor by

$$\xi_{00} = \eta/(N/3)\,(\overline{s_0^2}/M)\,\varrho Z_e(\lambda \Gamma_1 \Gamma_2)\exp\,(E/RT) = \eta'/Z_e\lambda \Gamma_1 \Gamma_2\,. \qquad (10)$$

Substitution of the known constants $(N, \overline{s_0^2}/M)$, empirical functions derived for E (Eq. (8)) and for ϱ (Eq. (9)), and of the viscosities corresponding to the chosen molecular weight (read off from the replotted experimental dependence $\log \eta$ vs $\log M$ according to the tabulated results[7-9]) gave the dependence $\log \eta'$ vs $\log M$ which after being adequately shifted both horizontally and vertically coincided very well with the dependence $\log (\lambda \Gamma_1 \Gamma_2)$ vs $\log \lambda$ for $s = 0.1$ (Fig. 3). By shifting the coordinates we obtained Z_e 89, in accordance with the relationship $\lambda = 1.52 \cdot 10^{-4}M$. Now it became possible, by substituting the values of $\log (\lambda \Gamma_1 \Gamma_2)$ for the respectively chosen molecular weights, to calculate from (10) the values of the characteristic frictional coefficient and to investigate its dependence on molecular weight (Fig. 4a). We can see that within a broad range of molecular weights ($\log M$ of 2.8 to 5.6)

TABLE I
Dependence of $\log (\lambda \Gamma_1 \Gamma_2)$ on $\log \lambda$ Calculated from Bueche's Function[4] for $s = 0.1$

$\log \lambda$	$\log (\lambda \Gamma_1 \Gamma_2)$				
	$K = 1$	$K = 1.5$	$K = 2$	$K = 2.5$	$K = 3$
−1.4	−1.394	−1.394	−1.394	−1.394	−1.394
−1.2	−1.191	−1.191	−1.190	−1.190	−1.190
−1.0	−0.986	−0.985	−0.985	−0.985	−0.985
−0.8	−0.777	−0.777	−0.777	−0.776	−0.776
−0.6	−0.564	−0.563	−0.563	−0.563	−0.563
−0.4	−0.343	−0.343	−0.342	−0.342	−0.342
−0.2	−0.111	−0.110	−0.109	−0.109	−0.109
0	0.138	0.139	0.140	0.140	0.141
0.2	0.414	0.416	0.417	0.417	0.418
0.4	0.729	0.732	0.733	0.734	0.734
0.6	1.106	1.110	1.112	1.114	1.114
0.8	1.571	1.581	1.587	1.592	1.595
1.0	2.131	2.157	2.174	2.186	2.196
1.2	2.769	2.813	2.843	2.866	2.885
1.4	3.449	3.517	3.563	3.597	3.623
1.6	4.142	4.228	4.292	4.340	4.378
1.8	4.849	4.939	5.009	5.066	5.114
2.0	5.570	5.659	5.728	5.785	5.834

this quantity really has a practically constant value of -10.62 with a scatter ± 0.06, i.e. ten times smaller than the scatter given for $\log \xi_0$ by Berry and Fox.

TABLE II

Dependence of $\log (\lambda \Gamma_1 \Gamma_2)$ on $\log \lambda$ Calculated from Bueche's Function[4] for $s = 0.2$

| $\log \lambda$	$\log (\lambda \Gamma_1 \Gamma_2)$				
	$K = 1$	$K = 1.5$	$K = 2$	$K = 2.5$	$K = 3$
-1.4	-1.393	-1.393	-1.393	-1.392	-1.392
-1.2	-1.189	-1.189	-1.188	-1.188	-1.188
-1.0	-0.983	-0.982	-0.981	-0.981	-0.981
-0.8	-0.772	-0.771	-0.770	-0.770	-0.770
-0.6	-0.555	-0.554	-0.553	-0.552	-0.552
-0.4	-0.328	-0.326	-0.325	-0.325	-0.324
-0.2	-0.084	-0.082	-0.081	-0.080	-0.080
0	0.185	0.188	0.189	0.190	0.190
0.2	0.500	0.503	0.505	0.506	0.507
0.4	0.898	0.903	0.906	0.907	0.908
0.6	1.434	1.451	1.461	1.468	1.474
0.8	2.087	2.130	2.159	2.181	2.198
1.0	2.787	2.858	2.907	2.944	2.974
1.2	3.504	3.592	3.653	3.702	3.742
1.4	4.222	4.332	4.405	4.460	4.504
1.6	4.927	5.054	5.143	5.211	5.264
1.8	5.634	5.762	5.857	5.933	5.995
2.0	6.349	6.474	6.567	6.643	6.706
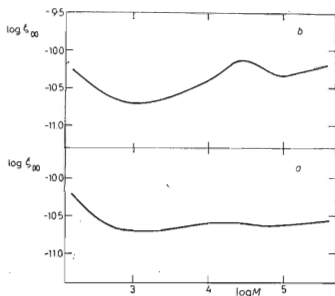
FIG. 4

Dependence of $\log \xi_{00}$ on $\log M$ Calculated by means of Bueche's Function (a) and Allen–Fox's Equation (b)

If the molecular weight is decreased (octamer to dimer), $\log \xi_{00}$ increases up to -10.22. The causes of such departure remain unclear.

As to the parameter Z_e, the value 89 determined by us differs fairly considerably from $Z_c' = 320$ determined by creep measurement. Berry and Fox[1] assume these quantities to be identical; however, so far no proof has been given for any polymer by direct determination of Z_e. The determined parameter $s = 0.1$ corresponds to a fairly low strength of the assumed entanglements in the melt; it could be related to the low kinetic rigidity of the siloxane chain.

It can be seen that Bueche's function can express very adequately the continuous change in the slope of the dependence of viscosity on molecular weight. The constant characteristic frictional coefficient thus obtained justifies the use of this function. We were interested to find out what difference will appear in the dependence $\log \xi_{00}$ vs $\log M$ if the semiempirical equation of Allen and Fox[4] is used for which a sharp change in the slope is assumed. Here, viscosity is given by

$$\eta = (N/6) X_c (X/X_c)^a \xi , \tag{11}$$

TABLE III
Dependence of $\log (\lambda \Gamma_1 \Gamma_2)$ on $\log \lambda$ Calculated from Bueche's Function[4] for $s = 0.3$

$\log \lambda$	$\log (\lambda \Gamma_1 \Gamma_2)$				
	$K = 1$	$K = 1.5$	$K = 2$	$K = 2.5$	$K = 3$
-1.4	-1.392	-1.392	-1.392	-1.391	-1.391
-1.2	-1.187	-1.187	-1.186	-1.186	-1.186
-1.0	-0.979	-0.978	-0.978	-0.977	-0.977
-0.8	-0.766	-0.765	-0.765	-0.764	-0.763
-0.7	-0.545	-0.543	-0.542	-0.542	-0.541
-0.4	-0.311	-0.308	-0.307	-0.306	-0.306
-0.2	-0.054	-0.051	-0.050	-0.049	-0.048
0	0.240	0.243	0.245	0.247	0.247
0.2	0.611	0.616	0.618	0.619	0.620
0.4	1.154	1.166	1.173	1.177	1.181
0.6	1.875	1.920	1.951	1.973	1.992
0.8	2.622	2.701	2.756	2.799	2.833
1.0	3.349	2.454	3.527	3.582	3.626
1.2	4.068	4.184	4.266	4.330	4.383
1.4	4.782	4.914	5.003	5.071	5.125
1.6	5.482	5.628	5.730	5.808	5.869
1.8	6.183	6.330	6.437	6.522	6.591
2.0	6.889	7.034	7.140	7.224	7.295

where $X = (\overline{s_0^2}/M)\, Z\varrho$. The exponent a should depend on the magnitude of X with respect to a certain critical value X_c; $a = 3\cdot4$ for $X > X_c$, and $a = 1$ for $X \leqq X_c$. According to this, the dependence of viscosity on molecular weight at a constant frictional factor should have a break at the critical value M_c.

After substitution of ξ from Eq. (7) into (11) the characteristic frictional factor is given by

$$\xi_{00} = \eta/(N/6)\,(\overline{s_0^2}/M)\varrho\, Z \exp\,(E/RT) \quad \text{for} \quad M \leqq M_c , \tag{12}$$

and

$$\xi_{00} = \eta Z_c^{2\cdot4}/(N/6)\,(\overline{s_0^2}/M)\,\varrho Z^{3\cdot4}\,\text{Jxp}\,(R/RT) \quad \text{foI} \quad M < M_c , \tag{13}$$

We used the above relationships to calculate the dependence of ξ_{00} on molecular weight similarly to the preceding case of Bueche's function; the critical value $Z_c = M_c/37$ was determined by using $M_c \cong 30000$ given by Kataoka and Ueda[7]. The characteristic frictional coefficient is not constant (Fig. 4b), $\log \xi_{00}$ varies from $-10\cdot2$ to $-10\cdot7$. If we assume that ξ_{00} should be independent of molecular weight, Fig. 4b demonstrates the limited use of Allen–Fox's equation for interpretation of the results obtained in the range of average molecular weights. This is particularly obvious at the critical molecular weight, where the curve exhibits a maximum. However, in the range of low and high molecular weights the relationship is still satisfactory and remains the only possible expression for a quantitative evaluation of the results. As to a similar practical application of Bueche's function which, as it seems, could be useful for a better interpretation of viscosity over the whole range of molecular weights, it will be the objective of forthcoming papers to check its validity for other polymers and to clarify the dependence of some of its constants on molecular parameters.

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