Estimation of the Inherent Friction Factor per Main-Chain Friction Unit of Liquid Low-Molecular-Weight Unsaturated Polyesters

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Synopsis

The temperature dependence (at 323–443 K) of the zero-shear viscosity η of about 30 non-fractionated samples of an unsaturated polyester ($300 < M_n < 1500$) was analyzed and the parameters of the Vogel equation describing the $\eta(T)$ dependence were estimated. Their dependence on the molecular weight is discussed. The inherent friction factor per main-chain friction unit, ξ_0, has been evaluated for $15 < Z_n < 70$ (where Z_n is the number-average number of main-chain friction units) and compared with the values available for other polymers.

INTRODUCTION

The analysis of the viscosity data for low-molecular-weight liquid polymers is usually based on the following equations[1]:

$$\eta = F(X)\xi \tag{1}$$

$$F(X) = (N_A/6)Z(\overline{Z}_0^2/M)v_2^{-1} \tag{2}$$

$$Z = M/m_a \tag{3}$$

$$\xi = \xi_0 \exp\left[1/\alpha(T - T_0)\right] \tag{4}$$

Here, $F(X)$ is the structure-dependent factor, ξ is the friction factor per main-chain atom (or atomic group), N_A is the Avogadro number, M and v_2 are, respectively, the molecular weight and specific volume of polymer. The symbol Z stands for the number of main-chain atoms and atomic groups considered as friction units, and m_a is the mean molecular weight per friction unit. $\overline{S}_0^2$ is the unperturbed mean-square radius of gyration. Its ratio to the molecular weight in the random-coil limit, $(\overline{S}_0^2/M)_\infty$, is a characteristic constant of the polymer. The inherent friction factor, ξ_0, is the value of ξ at $T \rightarrow \infty$. It is presumed to be independent of the chain length but to depend somewhat on the structure of the chain. The parameters α and T_0 of the Vogel equation [eq. (4)] are approximately constant at high molecular weights but need not be so at low M.[1]

The viscosity of liquid unsaturated polyesters at $M_n < 10^3$ is pro-

portional[2-4] to a rather high power of the molecular weight, $d \ln \eta / d \ln M$ being 4–8, although the molecular weights are in the range were proportionality of η to the first power of M is expected.[1] General reasons for this behavior have recently been discussed.[5] In order to obtain a better insight into the properties of these important resins and to learn more about the rheology of liquid short-chain polymers in general, we have decided to reanalyze the viscosity data published some time ago.[2]

In this paper we estimate the values of the parameters α and T_0 for about 30 polyester samples, explore their dependence on molecular weight, and calculate the inherent friction factor ξ_0 for $15 < Z_n < 70$, i.e., for the range of chain lengths which has not been investigated very much.[1] The results are compared with those obtained[3] for an unsaturated polyester of slightly different structure whose molecular weights were higher so that the molecular-weight dependence of α and T_0 was negligible.

EXPERIMENTAL

Unsaturated polyester samples[2] are products of the polycondensation of maleic and phthalic anhydrides with propane diol in proportions given in Table I. The samples were taken at different stages of the reaction and were characterized by the acid and hydroxyl numbers and by the number-average molecular weight M_n determined by the VPO method.[2]

Viscosity data at temperatures $T = 323, 353, 383, 413,$ and 443 K are given in Table II of Ref. 2.

RESULTS AND DISCUSSION

Estimation of the Parameters α and T_0 in Eq. (4)

The parameters α and T_0 are estimated by three methods, all of them being based on the equation

$$y \equiv (T_r - T)/\log(\eta/\eta_r) = 2.303 \, \alpha \, (T - T_0)(T_r - T_0) \qquad (5)$$

derived from eqs. (1) and (4) by Berry and Fox.[1] The viscosity is measured at several temperatures. One of them is chosen as the reference temperature T_r. The corresponding viscosity is η_r.

According to the first method (proposed by Berry and Fox[1]), the values of y are calculated according to the left-hand side of eq. (5) for several

TABLE I
Composition and the Mean Molecular Weight per Constitutional Unit
of Polyester Samples[2]

Sample	I	II	III	IV	V
MA[a] (mol)	2.3	2.3	2.3	2.3	2.3
PA[a] (mol)	1.0	1.0	1.0	1.0	1.0
PD[a] (mol)	3.46	3.52	3.59	3.68	3.84
m_0^b	166	164	162	159	155

[a] Abbreviations: MA=maleic anhydride, PA=phthalic anhydride, PD=propane diol.
[b] m_0 is the mean molecular weight per constitutional unit.

temperatures, plotted against $T_r - T$, and the intercept i and slope m of the linear dependence are determined. These are related[1] to T_0 and α by equations

$$\alpha = m^2/2.303i \tag{6}$$

$$T_0 = T_r + (i/m) \tag{7}$$

According to the second method, the values of y are plotted against T. As can be seen from eq. (5), the intercept at the T-axis gives directly T_0, and the slope of the linear plot is 2.303α $(T_r - T_0)$. This procedure may become less accurate if T_0 is much lower than the lowest temperature of measurement. This, fortunately, is not the case with unsaturated polyesters.

By plotting data according to the former or the latter method for two different reference temperatures, one should obtain identical results.

According to the third method, we choose two reference temperatures, $T_{r,i}$ (with $i = 1,2$). The corresponding viscosities are $\eta_{r,i}$. For a temperature T we calculate y_1 and y_2 according to the left-hand side of eq. (5). Since the ratio y_1/y_2 can be expressed by $(T_{r,2} - T_0)/(T_{r,1} - T_0)$ [it follows from eq. (5)], the estimation of T_0 yields

$$T_0 = \frac{(y_1/y_2)T_{r,2} - T_{r,1}}{(y_1/y_2) - 1} \tag{8}$$

The calculation is repeated for other pairs of η and T values, and the arithmetic mean of the T_0 values is taken. The parameter α is then evaluated evaluated according to eq. (5).

In this paper the second and third methods are used if viscosity measurements were carried out at four temperatures whereas the first method is employed if data were obtained at five temperatures (cf. Ref. 2). It is to be noticed that small inaccuracy in η or T makes the obtained values of α and T_0 inaccurate.

The Molecular-Weight Dependence of α and T_0

Since the temperature coefficients of $\bar{S}_0^2$ and v_2 in the structural factor $F(X)$, i.e., $d \ln \bar{S}_0^2/dT$ and $d \ln v_2/dT$, are of the order of magnitude of $10^{-3} \ \mathrm{deg}^{-1}$, it is the exponential term in eq. (4) which is the decisive contribution to the temperature coefficient of viscosity, $d \ln \eta/dT$. It then follows from eq. (1) that the ratio of viscosities, η_{T_1}/η_{T_2}, measured at two temperatures (T_1/T_2) should be invariant with respect to molecular weight if the parameters α and T_0 are independent of M.

Figure 1 shows that the ratio η_{T_1}/η_{T_2} for unsaturated polyesters increases with increasing M, which is unambiguous evidence that the parameters α and T_0 are functions of the molecular weight. This is confirmed by Figure 2 where the parameters estimated by the methods described above are plotted against M_n^{-1}. By plotting data in this way, we tentatively describe the molecular-weight dependence of α and T_0 by equations

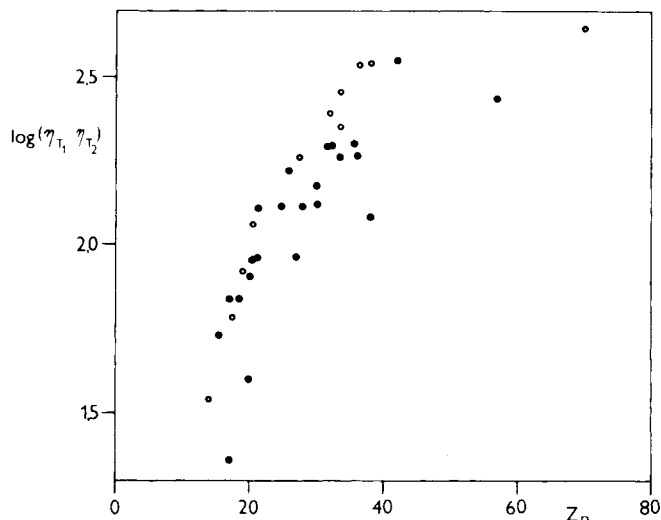$$2.303 \ \alpha = 2.303 \ \alpha^\infty + k_\alpha/M_n \tag{9}$$

Fig. 1. Plot of the logarithm of the ratio of viscosities at two temperatures (T_1, T_2) vs. the number-average number of main-chain friction units Z_n. Temperature: $T_1 = 353$, $T_2 = 443$ K. Data points: (○) I; (◑) II; (◓) III; (◑) IV; (●) V.

$$T_0 = T_0^\infty + k_T/M_n \qquad (10)$$

which are similar to those correlating the glass transition temperature and the expansion coefficient of liquid polymers with M.[1] According to these equations, α^∞ and T_0^∞ should be the limiting values at $M \to \infty$, but, unless the validity of these formulae is confirmed for $M > 10^3$, we consider α^∞ and T_0^∞ merely as empirical parameters. The values for the polyester samples are as follows: $T_0^\infty = 247$ K, $k_T = -9.7 \times 10^3$, $2.303 \, \alpha^\infty = 1.4 \times 10^{-3}$, $k_\alpha = 0.13$.
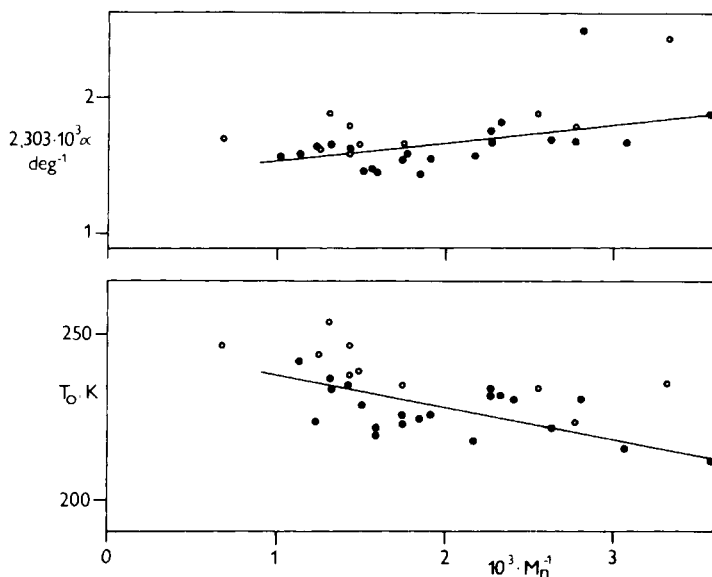

Fig. 2. Plot of the parameters α and T_0 vs. M_n^{-1}. Notation of points as in Figure 1.

By excluding molecular weight from eqs. (1)–(4) written for two temperatures (T_1, T_2), we obtain

$$\log \eta_{T_1} = \log \eta_{T_2} + \frac{1}{2.303 \, \alpha \, (T_1 - T_0)} - \frac{1}{2.303 \, \alpha \, (T_2 - T_0)} \qquad (11)$$

where molecular weight is only implicit in the parameters α and T_0. A plot according to eq. (11) is drawn in Figure 3. Data points for all samples overlap to form a single composite curve. This indicates that the scatter in Figure 2 is mainly due to the inaccuracy in M.

It follows from eqs. (1)–(4) that by subtracting from $\log \eta_T$ the values of $[2.303 \, \alpha \, (T - T_0)]^{-1}$ (taking into account the molecular-weight dependence of α and T_0), one obtains

$$\log A \equiv \log \eta_T - [2.303 \, \alpha \, (T - T_0)]^{-1}$$
$$= \log [(N_A/6)(\overline{S}_0^2/M)v_2^{-1}] + \log \xi_0 + \log Z$$

The values of $\log A$ should be independent of temperature. The plots of $\log A$ vs. T (Fig. 4) show no systematic trend, thus confirming the expectation.

Inherent Friction Factor

The inherent friction factor ξ_0 is assumed to be constant, at least for $Z > 80$. The Z values for unsaturated polyesters are calculated as $Z = M/m_a$, where $m_a = 29$ is the mean molecular weight per friction unit. In conformity with Ref. 1, the following main-chain atoms and groups are taken as friction units:—O—, —CO—, —CH$_2$, —CH=CH—, and —C$_6$H$_4$—. The Z_n values of unsaturated polyesters investigated here are lower
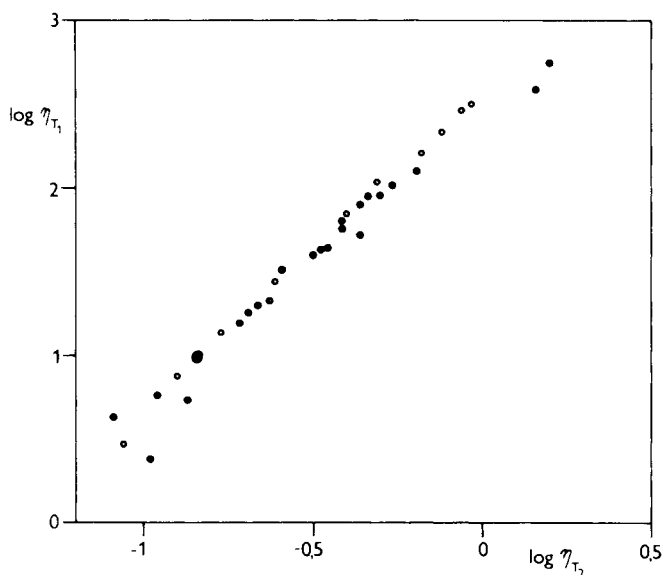

Fig. 3. Plot of the viscosity data according to eq. (11). Temperature: $T_1 = 353$, $T_2 = 443$ K. Notation of points as in Figure 1.
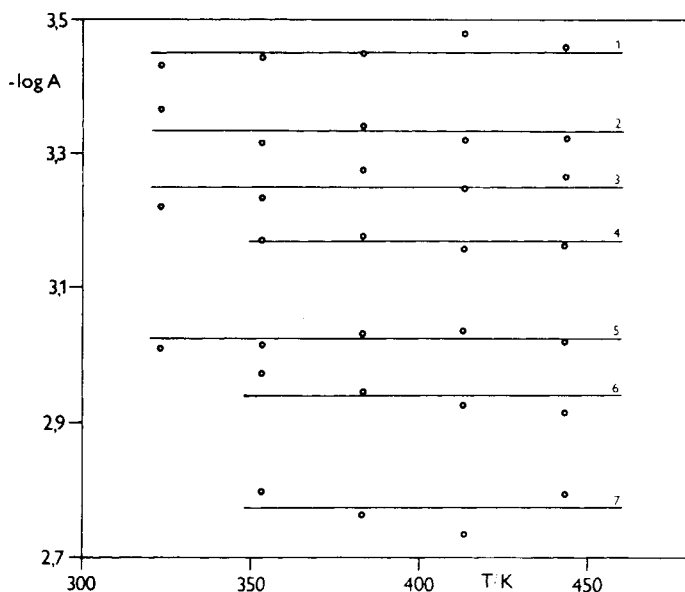
Fig. 4. Plot of log A [eq. (12)] vs. temperature. Curves 1–7 are for polyester samples I/2, I/3, I/6, I/9, I/7, I/8, and I/11.

than 80, so that the evaluation of log ξ_0 could allow a test of constancy of this parameter beyond the range of Z values investigated so far.

It is well known that short-chain polymers do not obey the random-flight chain statistics so that the ratio $\overline{S}_0^2/M$ depends on molecular weight and is lower than its limiting value, $(\overline{S}_0^2/M)_\infty = \lim_{M \to \infty} (\overline{S}_0^2/M)$. No data of this type are available for unsaturated polyesters. In order to estimate the magnitude of the ratio $Q = (\overline{S}_0^2/M)/(\overline{S}_0^2/M)_\infty$, we employ the equation

$$Q = 1 - \frac{3}{2}L_r^{-1} + \frac{3}{2}L_r^{-2} - \frac{3}{4}L_r^{-3}(1 - e^{-2L_r}) \tag{13}$$

advanced by Benoit and Doty[6] for the Kratky–Porod wormlike chain.[7,8] This chain is characterized by its persistence length $(1/2)\lambda^{-1}$ and the reduced contour length L_r

$$L_r = M/M_\lambda \tag{14}$$

where M_λ is molecular weight per Kuhn statistical segment length λ^{-1}.

For an unsaturated polyester of a slightly different composition, the parameters of the wormlike chain model have recently been estimated from intrinsic viscosity,[9] $(\overline{S}_0^2/M)_\infty = 0.067 \times 10^{-2}$ nm^2, $\lambda^{-1} = 0.92$ nm, $M_\lambda$nm, $M_\lambda = 211$, and we believe that the dependence of $\overline{S}_0^2/M$ on M calculated by means of them will satisfy the needs of the present calculation.

By substituting $Q \cdot (\overline{S}_0^2/M)_\infty$ for $\overline{S}_0^2/M$ into eq. (12), we obtain after rearrangement

$$\log \xi_0 = \log A - \log(Q \cdot Z) - \log[(N_A/6)(\overline{S}_0^2 M)_\infty v_2^{-1}] \tag{15}$$

The approximate correction factor Q is computed according to eq. (13). The molecular-weight dependence of the specific volume is so small that it can be fully neglected. The value 0.820 cm^3/g is substituted for v_2.

The viscosity of low-molecular-weight liquid polymers should be correlated[1] with the weight-average molecular weight M_w. This quantity cannot be directly measured with unsaturated polyesters but can be estimated according to equations

$$q = 1 - P_n^{-1} \tag{16}$$

$$P_w = P_n (1 + q) \tag{17}$$

which follow from the statistical theory of polycondensation[10] if the initial mole ratio of hydroxyl and carboxyl groups is unity. The symbols P_w and P_n stand for the weight-average and number-average degree of polymerization, respectively, and q is the degree of conversion.

Since the initial mole ratio of the diol and the acid anhydrides was not far from unity (1.05 – 1.16), we employ eqs. (16) and (17) to estimate P_w and Z_w. The mean molecular weights m_0 per constitutional unit needed to calculate P ($P = M/m_0$) are given in Table I.

Figure 5 represents a plot of log ξ_0 calculated according to eq. (15) vs. Z_n with the values of Z_n [Fig. 5(a)] and Z_w [Fig. 5(b)]. The scatter of the data points is mainly due to the inaccuracy of the α and T_0 values. A difference of about 10% in α and of less than 10 K in T_0 produces a difference of less than 10% in $[2.303 \, \alpha(T - T_0)]^{-1}$ but of about 0.3 in log ξ_0.

A slight decrease in log ξ_0 with increasing chain length is indicated by the data at $Z_n < 20$ (Fig. 5), but the values of log ξ_0 at $Z_n \gtrsim 25$ seem to be
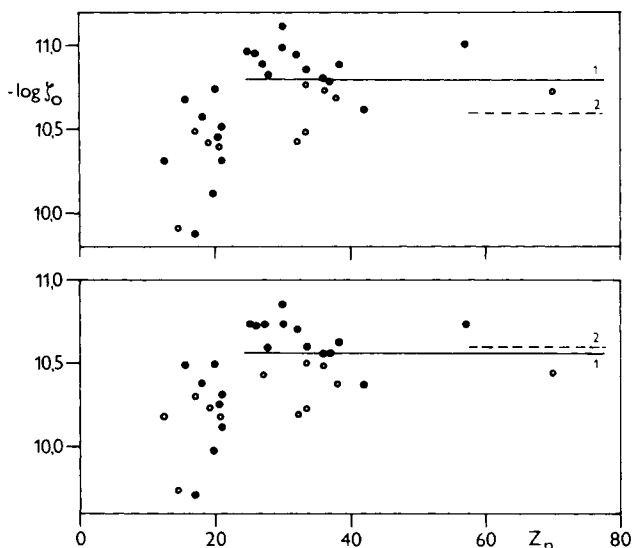

Fig. 5.   Plot of the logarithm of the inherent friction factor ξ_0 vs. the number-average number of main-chain friction units Z_n. Notation of data points as in Figure 1. Values of log ξ_0 calculated according to eq. (15) with Z_n (a) or Z_w (b). Lines 1 and 1' correspond to the arithmetic means for $Z_n > 25$; line 2 corresponds to log $\xi_0 = -10.6$ (cf. Ref. 3).

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independent of Z_n within the experimental uncertainty ($\pm$ 0.3). The arithmetic mean for this range is log ξ_0 = -10.56 [according to Fig. 5(a)] or -10.80 [Fig. 5(b)] but only slightly higher results (-10.43 and -10.68) would be obtained if all data were included into the averaging procedure. All these values are in fair agreement with log ξ_0 = -10.6 estimated recently[3] for another unsaturated polyester.

Berry and Fox[1] have collected the ξ_0 values for several polymers and pointed out that the highest ones ($10^{-12} < \xi_0 < 10^{-11}$) correspond to unsubstituted polymer chains (polyethylene, polybutadiene) whereas the lowest ones belong to polymers with bulky side chains such as esters of poly(methacrylic acid). It is remarkable that the ξ_0 value for unsaturated polyesters ($\xi_0 \simeq 3 \times 10^{-11}$) is close to the upper limit of the above interval, although the polyester chains are structurally not very similar to those of polyethylene or polybutadiene, except in one respect: they are unsubstituted. This factor seems to be more important than the presence of double bonds, phenylene and ester groups which, in principle, could lead to different types and intensities of the intramolecular interactions and thus affect the magnitude of ξ_0.

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