

## UNUSUALLY HIGH VALUES OF THE QUOTIENT $d \ln \eta / d \ln M$ OF SOME LOW-MOLECULAR-WEIGHT LIQUID POLYMERS

Miloslav BOHDANECKÝ<sup>a</sup>, Alois KAŠTÁNEK<sup>b</sup>, František LEŠEK<sup>b</sup>

<sup>a</sup> *Institute of Macromolecular Chemistry,*

*Czechoslovak Academy of Sciences, 162 06 Prague 6 and*

<sup>b</sup> *Research Institute for Synthetic Resins and Lacquers, Pardubice*

Received April 23th, 1985

*Dedicated to Dr B. Sedláček on the occasion of his 60th birthday.*

Unusually high values of the quotient  $d \ln \eta / d \ln M \equiv a$  (where  $\eta$  is viscosity and  $M$  is molecular weight) found for some low-molecular-weight liquid polymers ( $4 \leq a \leq 8$ ) are discussed in terms of the theory of flow processes of polymeric liquids. The effect is assigned mainly to the dependence on the chain length of the friction factor per main chain atom or atomic group but deviations of short chains from the conformation of random coils can also contribute significantly. The variation of the quotient  $a$  with temperature, however, is due to the former factor only.

Basing on the suggestion by Ewell<sup>1</sup>, the theory of flow processes in liquid polymers<sup>2</sup> considers the zero-shear viscosity,  $\eta$ , to be a product of two factors, *viz.*, of the structural factor,  $F(X)$ , and of the friction factor per main chain atom or atomic group,  $\zeta$ ,

$$\eta = F(X) \cdot \zeta, \quad (1)$$

where

$$F(X) = (N_A/6) X_c (X/X_c)^a, \quad (2)$$

$$X = Z \overline{S}_0^2 / M v_2, \quad (3)$$

$$Z = M / m_a, \quad (4)$$

and

$$\zeta = \zeta_0 \exp [1/\alpha(T - T_0)]. \quad (5)$$

Here,  $N_A$  is the Avogadro number,  $M$  is the polymer molecular weight,  $\overline{S}_0^2$  is the unperturbed mean-square radius of gyration of the polymer molecule,  $v_2$  is the specific volume of the liquid polymer,  $Z$  is the number of main chain atoms (or groups) of the mean molecular weight  $m_a$  each,  $\zeta_0$  is the inherent friction factor per main chain atom,  $\alpha$  and  $T_0$  are empirical parameters. The symbol  $X_c$  stands for the

“critical” value of the combined variable  $X$  at which, due to the onset of entanglement of polymer chains, the logarithmic plot of  $\eta$  vs  $M$  shows a more or less abrupt change in the slope.

The quotient  $a \equiv \text{dln } \eta / \text{dln } M$  equals 3.4 at  $X > X_c$  and is expected to be unity at  $X < X_c$ . In the latter range, however, the quotient sometimes depends on the chain length and is  $1 \leq a \leq 2.5$  (refs<sup>2,3</sup>). This fact is assigned to a molecular-weight dependence of the friction factor ( $\zeta$ ), so that on recalculating isothermal viscosity data to the limiting (constant) value of the friction factor, the proportionality of viscosity and molecular weight is obtained<sup>2</sup>.

Unusually high values of the quotient ( $4 \leq a \leq 8$ ) have been observed in the low-molecular-weight region with unsaturated polyesters<sup>4-6</sup> ( $300 \leq M_n \leq 10^3$ ), polyesters of phthalic acid<sup>7</sup> ( $300 \leq M_n \leq 700$ ), and with epoxy resins<sup>8</sup> ( $M_c < 2 \cdot 10^3$ ), and a decrease of the quotient with increasing temperature has been reported in some cases<sup>4,8</sup>.

In the present paper we try to explain this behaviour by taking into account the molecular-weight dependence not only of the friction factor ( $\zeta$ ) but also of some other factors in the above equations which, for high molecular weights, can be assumed to be invariant with respect to  $M$ .

#### THEORETICAL

According to Eqs (1) to (5), the viscosity at  $X < X_c$  should be proportional to the number of polymer chains per  $\text{cm}^3$  (i.e.,  $N_A/Mv_2$ ), mean-square distance of the frictional centres from the centre of mass (i.e., to  $\bar{S}_0^2$ ), number  $Z$  of main chain atoms or atomic groups acting as frictional centres, and to the mean friction factor ( $\zeta$ ). The latter is a characteristic of intermolecular forces between segments of different chains. The proportionality to molecular weight has been predicted for the viscosity of non-interacting and free-draining coils in solution<sup>9</sup>, and the free-draining behaviour of liquid polymers is explained by the intramolecular hydrodynamic interaction being screened by the macromolecular surroundings<sup>2</sup>.

If polymer chains are short, several factors in Eqs (1) to (5) become dependent on molecular weight. The specific volume,  $v_2$ , is higher than its limiting value because of the end-group effect. The ratio  $\bar{S}_0^2/M$  in Eq. (3) is lower than its limiting value  $(\bar{S}_0^2/M)_\infty$ . The parameters  $\alpha$  and  $T_0$  vary considerably with  $Z$  at  $Z \leq 500$  (ref.<sup>2</sup>). One also could speculate about a dependence on molecular weight of the inherent friction factor,  $\zeta_0$ . This, however, has been shown to be constant at  $Z > 80$  (ref.<sup>2</sup>), and an analysis<sup>10</sup> of the data for unsaturated polyesters has detected no significant deviations from this rule even at  $25 < Z < 80$ .

Taking all these factors into account, one obtains from Eq. (1) for  $X < X_c$ ,

$$a = 1 - a_1 + a_2 + a_3, \quad (6)$$

where

$$a_1 = d \ln v_2 / d \ln M, \quad (7)$$

$$a_2 = d \ln \bar{S}_0^2 / d \ln M, \quad (8)$$

$$a_3 = \frac{1}{\alpha(T - T_0)} \left[ \frac{1}{T - T_0} \cdot \frac{dT_0}{d \ln M} - \frac{d \ln \alpha}{d \ln M} \right]. \quad (9)$$

The quotients  $a_1$ ,  $a_2$  and  $a_3$  are now discussed in detail.

### *Specific Volume*

The dependence of the specific volume on molecular weight can be described by the equation<sup>2</sup>

$$v_2 = v_2^\infty + k_1/M, \quad (10)$$

so that

$$a_1 = -[1 + (v_2^\infty/k_1)M]^{-1} \quad (11a)$$

and

$$\lim_{M \rightarrow \infty} a_1 = 0. \quad (11b)$$

The convergence of  $a_1$  to its limiting value depends on the value of  $v_2^\infty/k_1$ . Typically,  $v_2^\infty/k_1 \cong 0.1$  so that  $a_1 = -0.1$ ,  $-0.01$ , and  $-0.001$  for  $M$   $10^2$ ,  $10^3$  and  $10^4$ , respectively.

### *Mean-Square Radius of Gyration*

The mean-square radius of gyration,  $\bar{S}_0^2$ , appears in Eq. (3) because, according to the theory of Debye<sup>9</sup>, the viscosity of free-draining coils is proportional to the sum of the average square of the distance of one group from the centre of gravity,  $\sum_j \langle S_j^2 \rangle$ , in other words to the mean-square radius of gyration,

$$\bar{S}_0^2 = \frac{1}{n} \sum_j S_j^2.$$

The sum depends on the distribution function of main chain atoms around the centre of gravity. For chains long enough to assume the conformation of random coils ( $n \rightarrow \infty$ ),  $\bar{S}_0^2$  is proportional to the number of main chain bonds,  $n$ . For short chains the distribution function is different and the ratio  $\bar{S}_0^2/n$  is a function of  $n$ . We now compare the value of  $a_2$  for several chains at a finite number of bonds.

The simplest model is the freely jointed chain composed of  $n$  main chain bonds whose length,  $l$ , is fixed but whose orientation is random. For this model<sup>11</sup>,

$$\overline{S}_0^2 = (nl^2/6)(n+2)/(n+1), \quad (12)$$

so that

$$a_2 = 1 - \frac{n}{(n+1)(n+2)} \quad (13)$$

Fig. 1 shows that for the freely jointed chain, the quotient  $a_2$  only very slightly increases with the number of bonds.

Relations between  $\overline{S}_0^2$  and  $n$  for other models (*e.g.* free-rotating chain, chain with independent rotations, *cf.*<sup>12</sup>) are rather involved, so we prefer evaluating  $a_2$  from the results of theoretical calculations for several real chains with fixed bond length and angles, and with interdependent rotations around the main chain bonds. The dependences of the mean-square end-to-end distance,  $\overline{R}_0^2$ , on the number of bonds are available in graphs only but Orofino<sup>13</sup> succeeded to find a simple analytical form

$$\overline{R}_0^2/nl^2 = C_\infty(1 - B/n), \quad (14)$$

where  $B$  is a parameter and  $C_\infty$  is the characteristic ratio,

$$C_\infty = \lim_{n \rightarrow \infty} (\overline{R}_0^2/nl^2). \quad (15)$$

Eq. (14) reproduces the original values with a precision better than 2%. For the mean-square radius of gyration, Orofino obtained

$$\overline{S}_0^2 = (C_\infty/6)nl^2 \left(1 - \frac{3B-1}{n}\right). \quad (16)$$

The quotient  $a_2$  calculated from Eq. (16) is

$$a_2 = \left(1 - \frac{3B-1}{n}\right)^{-1}. \quad (17)$$

Fig. 1 represents the dependence on the number of bonds of the quotient  $a_2$  for  $\alpha$ -ethyl- $\omega$ -ethoxy-poly(oxyethylene) and poly(oxyethylene)<sup>14</sup> ( $C_\infty = 4.0$ ), nylon 66 (ref.<sup>14</sup>) ( $C_\infty = 6.1$ ), and polymethylene<sup>14</sup> ( $C_\infty = 6.7$ ). The quotient is a strongly decreasing function of the number of bonds, the decrease being the steeper the higher the chain stiffness characterized by the value of  $C_\infty$ . At  $n > 100$  (200),  $a_2$  is lower than 1.2 (1.1).

Let us compare these findings with a general prediction based on the Kratky–Porod worm-like chain model<sup>15,16</sup> which is frequently used to mimic the stiff and/or short-polymer chains. It is characterized by the reduced contour length,  $L_r$ , and the persistence length  $b$ . The former is defined as

$$L_r = M/M_L \lambda^{-1} = M/6M_L^2(\overline{S_0^2}/M)_\infty, \quad (18)$$

where  $M_L$  is the molecular weight per unit contour length and  $\lambda^{-1}$  is the Kuhn statistical segment length,

$$\lambda^{-1} = 2b. \quad (19)$$

Benoit and Doty<sup>12</sup> have shown that the mean-square radius of gyration depends on  $L_r$  according to the equation

$$\overline{S_0^2}/L_r = (\overline{S_0^2}/L_r)_\infty [1 - \frac{1}{2}L_r^{-1} + \frac{1}{2}L_r^{-2} - \frac{1}{2}L_r^{-3}(1 - e^{-2L_r})]. \quad (20)$$

The quotient  $a_2$  is readily obtained from Eq. (20) as

$$a_2 = 1 + \frac{\frac{1}{2}L_r^{-1}[1 - L_r^{-1}(2 + e^{-2L_r}) + \frac{1}{2}L_r^{-2}(1 - e^{-2L_r})]}{1 - \frac{1}{2}L_r^{-1}[1 - L_r^{-1} + \frac{1}{2}L_r^{-2}(1 - e^{-2L_r})]}, \quad (21a)$$

$$\lim_{L_r \rightarrow \infty} a_2 = 1. \quad (21b)$$

It is a decreasing function of  $L_r$ , being  $1.69 > a_2 > 1.14$  at  $1 \leq L_r \leq 10$  and approaching its limiting value at  $L_r > 100$ . Since the chain length corresponding to a fixed value of  $L_r$  (say 10) is the lower, the lower  $\lambda^{-1}$ , it is clear that the quo-

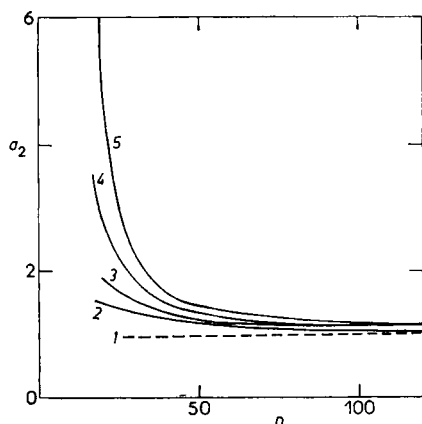


FIG. 1

Dependence of the quotient  $a_2$  on the number of main chain bonds. Curve 1 freely jointed chain (Eq. (13)), 2 to 5 real chains ((Eq. (17) with  $B$  2.5, 3.4, 4.6, and 5.6). Details in text

tient will sooner be close to unity for polymers with low  $\lambda^{-1}$  values. This is consistent with the results in Fig. 1.

### Parameters $\alpha$ and $T_0$

As has been emphasized in ref.<sup>2</sup> and confirmed in the study of unsaturated polyesters<sup>10</sup>, it is difficult to obtain accurate values of the parameters  $\alpha$  and  $T_0$  for low-molecular-weight polymers and to find reliable expressions for their dependences on  $M$ . Equations

$$\alpha = \alpha^\infty + k_\alpha/M, \quad (22)$$

$$T_0 = T_0^\infty + k_T/M \quad (23)$$

(with  $a^\infty = \lim_{M \rightarrow \infty} \alpha$  and  $T_0^\infty = \lim_{M \rightarrow \infty} T_0$ ) are used because of their similarity to equations describing the effect of molecular weight on the expansion coefficient of liquid polymers and the glass-transition temperature<sup>8,10</sup>.

The quotients  $d \ln \alpha / d \ln M$  and  $d T_0 / d \ln M$  are

$$d \ln \alpha / d \ln M = -[1 + (\alpha^\infty / k_\alpha) M]^{-1}, \quad (24)$$

$$d T_0 / d \ln M = -k_T / M. \quad (25)$$

Their limiting values at  $M \rightarrow \infty$  are zero, and their convergence depends on the values of  $\alpha^\infty / k_\alpha$  and  $k_T$ , respectively.

To illustrate the situation at this point, we calculate the quotients  $d \ln \alpha / d \ln M$ ,  $d T_0 / d \ln M$ , and  $a_3$  according to Eqs (24), (25) and (11a) with  $k_T = -9.7 \cdot 10^3$ ,  $T_0^\infty = 247$  K,  $k_\alpha = 0.13$ , and  $\alpha^\infty = 6.1 \cdot 10^{-4}$ , corresponding to an unsaturated polyester investigated in ref.<sup>10</sup>. The results for  $T$  323 and 443 K are represented in Fig. 3 (curves 2 and 3). The molecular weight has been recalculated to the number of main chain bonds  $n$  (upper scale) according to  $n = M / m_b$ , where  $m_b$  (20.9) is the molecular weight per main chain bond.

The quotient  $d \ln \alpha / d \ln M$  is negative whereas  $d T_0 / d \ln M$  is positive but their contributions to  $a_3$  according to Eq. (9) are of the same sign.

### DISCUSSION

Fig. 3 (curve 1) shows that the quotient  $a_1$  is negligible at  $M > 10^3$  and nearly so at  $M < 10^3$ , so that its contribution to the quotient  $a$  is within the limits of error of the latter.

The relevance of the quotient  $a_2$  (Figs 2 and 3) depends not only on the chain

length, but also on the chain stiffness. It is always much higher than  $a_1$  but lower than  $a_3$ .

The curves in Fig. 3 have reference to an unsaturated polyester and would have a different shape with other polymers. We are aware of no data allowing an estimation of  $a_3$  for polymers represented in Fig. 1. On the other hand, nothing is known about the molecular-weight dependence of  $\bar{S}_0^2/M$  for polyesters so that a corresponding curve cannot be drawn in Fig. 1. The characteristic ratio of unsaturated polyesters being<sup>17</sup>  $C_\infty = 3.4 - 4$ , we believe that curve 2 or 3 in Fig. 1 can be used for semiquantitatively assessing the relative importance of the quotients  $a_2$  and  $a_3$  in this particular case.

According to these curves,  $a_2$  is lower than 1.25 at  $n > 50$  (i.e.  $M > 10^3$ ) and does not exceed  $a_2 = 2$  even at  $n = 20$  ( $M = 400$ ). It cannot, therefore, fully account for the high value of the quotient  $a$  mentioned in the introduction for polyesters although it can be a relevant contribution to the latter at low chain lengths.

The situation will be different with other polymers but unless the molecular-weight dependence of the quotient  $a_3$  is too different, the quotient  $a_3$  will probably be the most important factor contributing to  $a$ .

Fig. 3 shows that with an increase in temperature, the quotient  $a_3$  becomes lower. The other terms ( $a_1, a_2$ ) are nearly independent of temperature, so that it is the variation of  $a_3$  with  $T$  which is responsible for the decrease in  $a$ . It can happen, however, that the term  $a_2$  will become comparable to  $a_3$  at higher temperatures.

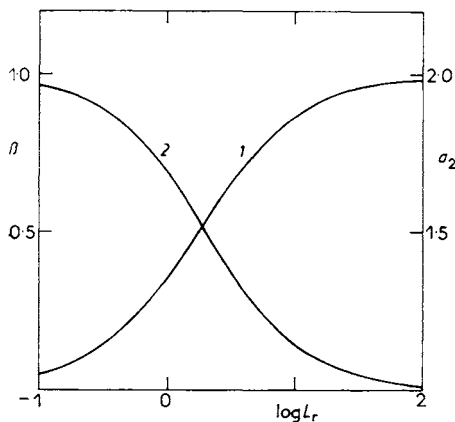


FIG. 2

Dependence of the ratio  $\bar{S}_0^2/L_r$  and the quotient  $a_2$  on the reduced contour length of the worm-like chain model. Curve: 1  $\beta = (\bar{S}_0^2/L_r)/(\bar{S}_0^2/L_r)_\infty$ , 2 quotient  $a_2$

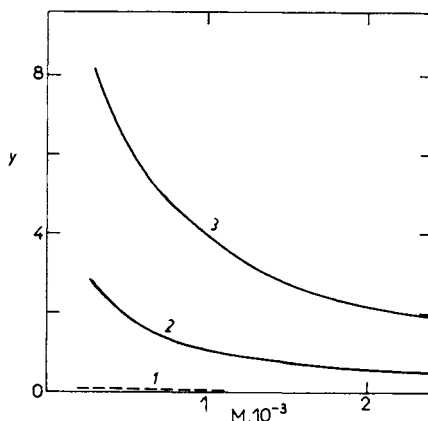


FIG. 3

Dependence of the quotients  $a_1$  and  $a_3$  on the molecular weight. Curve 1  $y = -a_1$ ; curves 2, 3  $y = a_3$  calculated by means of Eqs (24), (25) and (11) for  $T$  443 and 323 K. Details in text

The previous discussion rests on the assumption of monodispersity of polymer samples with respect to molecular weight. Polydispersity makes the analysis impossible because its effect on the parameters  $\alpha$  and  $T_0$ , which essentially are empirical quantities, is unknown. It is, however, not difficult to discuss this effect, if the quotient  $a$  is equal or close to unity.

In this case, the melt viscosity should be correlated with the weight-average molecular weight  $M_w$ . If this cannot be measured so that the number average value  $M_n$  has to be used, several possibilities exist for the relationship between the quotient  $a_n$  of the correlation of  $\eta$  with  $M_n$  and the quotient  $a$  of the correlation with  $M_w$ .

If the polydispersity index  $M_w/M_n$  is the same for all samples, the quotient  $a_n$  is equal to  $a$ . If, however, the polydispersity systematically varies with increasing  $M$ , the value of  $a_n$  can be higher or lower than  $a$ , depending on the trend of the variation.

Let us discuss a special case. In some papers<sup>4,5</sup> mentioned in the introduction, the samples were non-fractionated products of polycondensation, taken at different stages of the reaction and probably differing in polydispersity. In the following paragraphs, we shall show that this fact can affect the quotient  $a$  in a significant way. If the initial mole ratio of the reaction components is unity, the following equations, based on the statistical theory of polycondensation, are valid<sup>18</sup>:

$$q = 1 - P_n^{-1}, \quad (26)$$

$$P_w = P_n(1 + q), \quad (27)$$

where  $P_w$  and  $P_n$  are, respectively, the weight-average and number-average degree of polymerization. The polydispersity index  $P_w/P_n$  is an increasing function of  $q$ , the degree of conversion, and converges to  $P_w/P_n = 2$  at  $q \rightarrow 1$ .

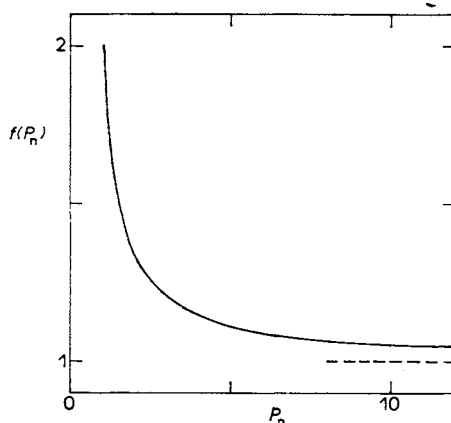


FIG. 4  
Polydispersity function  $f(P_n)$  calculated according to Eq. (31). Broken line:  $\lim_{q \rightarrow 1} f(P_n) = 1$



Let us write

$$\eta = K_T P_w^a. \quad (28)$$

If we substitute for  $P_w$  according to Eqs (26) and (27), we obtain

$$\eta = K_T (2P_n - 1)^a. \quad (29)$$

The quotient  $a_n$  then is

$$a_n \equiv \frac{d \ln \eta}{d \ln P_n} = a f(P_n), \quad (30)$$

where

$$f(P_n) = (1 - 1/2P_n)^{-1}. \quad (31)$$

Fig. 4 shows that, at low degrees of polymerization, the polydispersity has a larger effect on the quotient  $a_n$  although the polydispersity index is closer to unity. At higher degrees of polymerization, the values of  $f(P_n) \cong \lim_{q \rightarrow 1} f(P_n) = 1$  so that  $a_n \cong a$ .

According to Eq. (30),  $a_n$  is the product of the "correct" quotient  $a$  and of the function  $f(P_n)$ . Fig. 4 shows that, due to a systematic increase of polydispersity with molecular weight, the quotient  $a_n$  at low degrees of polymerization can be increased by 50 or 100% above the "correct" value,  $a$ . It is clear that the variation of polydispersity with molecular weight should be considered whenever the viscosity data of low-molecular-weight polydisperse polymers are correlated with  $P_n$ .

#### REFERENCES

1. Ewell R. H.: *J. Appl. Phys.* 3, 252 (1938).
2. Berry G. C., Fox T. G.: *Advan. Polym. Sci.* 5, 261 (1968).
3. Semjonov V.: *Advan. Polym. Sci.* 5, 387 (1968).
4. Lešek F., Kletečková Z., Skopalík J., Novák M.: *Chem. Prům.* 32, 130 (1982).
5. Bohdanecký M., Tamchyna J., Zvonář V.: *Chem. Prům.* 8, 382 (1958).
6. Kaštánek A., Zelenka J., Hájek J.: *J. Appl. Polym. Sci.* 29, 447 (1984).
7. Neumann G., Schimpfle H. U., Becker R.: *Plaste Kaut.* 24, 27 (1977).
8. Kaštánek A.: Unpublished results.
9. Debye P.: *J. Chem. Phys.* 14, 636 (1946).
10. Kaštánek A., Balcar M., Bohdanecký M., Lešek F.: *J. Appl. Polym. Sci.*, in press.
11. H. Yamakawa: *Modern Theory of Polymer Solutions*. Harper and Row, New York 1971.
12. Benoît H., Doty P.: *J. Phys. Chem.* 57, 958 (1953).
13. Orofino T. A.: *Polym. Preprints* 9, 260 (1968).
14. Flory P. J.: *Statistical Mechanics of Chain Molecules*. Interscience, New York 1969.
15. Kratky O., Porod G.: *Rec. Trav. Chim. Pays-Bas* 68, 1106 (1949).
16. Porod G.: *Monatsh.* 80, 251 (1949).
17. Kaštánek A., Bohdanecký M.: *Eur. Polym. J.*, in press.
18. Peebles L. H., jr: *Molecular Weight Distribution in Polymers*. Interscience, New York 1971.

Translated by L. Kopecká.