

# The Viscosity of an Unsaturated Polyester

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## Synopsis

The zero-shear viscosities of the fractions of an unsaturated polyester were determined by using a rotation viscosimeter with cone-and-plate measuring system. The polyester was prepared by the generally known melt condensation of maleic anhydride, phthalic anhydride, ethylene glycol, and cyclohexanol. The viscosity-temperature relationship and the viscosity-molecular weight relationship are given. The low value of the critical molecular weight as well as rather high value of the inherent friction factor are probably caused by high forces between polar groups of the chains of an unsaturated polyester.

## INTRODUCTION

To relate measurable viscoelastic constants, such as the zero shear viscosity  $\eta$ , to molecular parameters, such as the dimensions of the polymer coil and intermolecular friction constant, is a major aim of the physical investigation of polymer melts. A great deal of the results of investigations on the viscosity is reviewed in Refs. 1 and 2.

According to the theory of the flow of liquids<sup>3-5</sup> consisting of chain polymers, the viscosity  $\eta$  can be considered to be the product of two factors, a structure sensitive factor  $F(Z)$  dependent primarily on number of atoms (or groups of atoms)  $Z$  in the chain backbone and a temperature or density dependent friction factor per chain atom (or group of atoms)  $\zeta$ :

$$\eta = F(Z)\zeta \quad (1)$$

$F(Z)$  is defined, in accord with Bueche,<sup>6</sup> by

$$F(Z) = (N_A/6)(\bar{s}_0^2/M)(Z/Z_c)^{a-1}(Z/v) \quad (2)$$

$$a = 3.4, Z \geq Z_c$$

$$a = 1.0, Z < Z_c$$

$N_A$  is the Avogadro number,  $\bar{s}_0^2$  is the unperturbed mean square radius of gyration,  $M$  is the molecular weight,  $Z_c$  is the critical value of  $Z$ , and  $v$  is the specific volume.

According to the free volume concept of the flow the temperature dependence of the viscosity is given<sup>7-11</sup> by

$$\eta = Ae^{B/f} \quad (3)$$

where  $B$  is the temperature-independent constant, a parameter  $A$  is almost temperature independent but depends on the molecular weight, and  $f$  is the fractional free volume at temperature  $T$ .

Equation (3) is practically identical with the Vogel empirical three-parameter equation expressing dependence of the viscosity  $\eta$  on temperature  $T^{2,12}$ :

$$\eta = Ae^{1/\alpha(T-T_0)} \quad (4)$$

where constants  $\alpha$  and  $T_0$  are temperature-independent but can depend on molecular weight (over the low molecular weight region).

Taking eqs. (1), (3), and (4) into account, the temperature dependence of the friction factor  $\zeta$  is controlled through its dependence on the fractional free volume:

$$\ln \zeta = \ln \zeta_0 + B/f \quad (5)$$

or

$$\ln \zeta = \ln \zeta_0 + 1/\alpha(T - T_0) \quad (6)$$

The inherent friction factor  $\zeta_0$  is presumed to be constant, independent of molecular weight and temperature. It can be calculated from a parameter  $A$  [ $A = F(Z)\zeta_0$ ].

## EXPERIMENTAL PROCEDURE

**Preparation of the Polyester.** Unsaturated polyester was prepared by melt condensation of ethylene glycol (740 g), maleic anhydride (472.5 g), and phthalic anhydride (1044 g) in atmosphere of nitrogen at 220°C. When the acid value 62.2 mg KOH/g had been reached, cyclohexanol (160 g) was added dropwise for 15 min. At last, evacuation was carried out (15 min).

**Preparation of the Fractions.** Fractions were prepared by a precipitation fractionation of the polyester that is exactly described in Ref. 13.

**Molecular Weight Determination.** Determination of the number-average molecular weights  $\bar{M}_n$  was carried out by vapor pressure osmometry as exactly described in Ref. 13.

**Viscosity Measurements.** A rotation viscosimeter Rheotest 2 with cone-and-plate measuring system was used for our measurements. A plate is electrically heated and its temperature regulation is performed by means of a transistor regulator TRS 12. The temperature-measuring element is a platinum resistance thermometer Pt 100.

## RESULTS

### Dependence of the Viscosity on Temperature and Molecular Weight

Dependences of  $\log \eta$  on  $1/T$  are given for several  $\bar{M}_n$  in Figure 1. Dependences of  $\log \eta$  on  $\bar{M}_n^{1/2}$  are given for several  $T$  in Figure 2.

Dependence of the viscosity  $\eta$  (mPa·s) on temperature  $T(K)$  and molecular weight  $\bar{M}_n$  can be expressed by eq. (7) applicable for  $\bar{M}_n > 700$ :

$$\log \eta = K(T) + C\bar{M}_n^{1/2} \quad (7)$$

where  $C = 0.05$ .

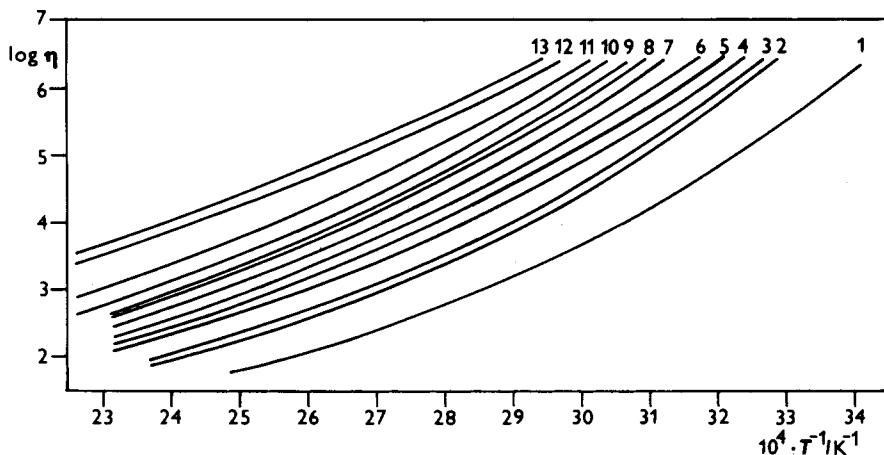


Fig. 1. Dependence of  $\log \eta$  on  $T^{-1}$  for unsaturated polyester fractions 1-13 of  $\bar{M}_n$  390, 450, 590, 500, 680, 1030, 1600, 2200, 2040, 2700, 2510, 2930, and 4390.

$K(T)$  is given by eq. (8):

$$K(T) = K(T \rightarrow \infty) + 1/2.303\alpha(T - T_0) \tag{8}$$

where  $T_0 = 233.2$  K,  $\alpha = 7.0 \times 10^{-4}$  K $^{-1}$ ,  $K(T \rightarrow \infty) = -2.45$ .

Parameters  $\alpha$  and  $T_0$  were determined by the graphical treatment of the experimental values according to Berry and Fox,<sup>2,14</sup> and they are applicable for  $320$  K  $< T < 430$  K and  $700 < \bar{M}_n < 4400$ .

Dependences of  $\log \eta$  on  $\log \bar{M}_n$  for several  $T$  and dependence of  $\log \eta$  on  $\log \bar{M}_w$  for  $T = 400$  K are shown in Figure 3. Calculations of  $\bar{M}_w$  of the fractions are given in Ref. 13.

It is possible to consider that the curves exhibit two regions, with slopes  $a_n \doteq 1.5$  ( $700 < \bar{M}_n < 1780$ ) and  $a_n \doteq 3.4$  ( $\bar{M}_n > 1780$ ). A critical value of  $\log \bar{M}_{nc} \doteq 3.25$  ( $\bar{M}_{nc} \doteq 1780$ ) may be estimated.

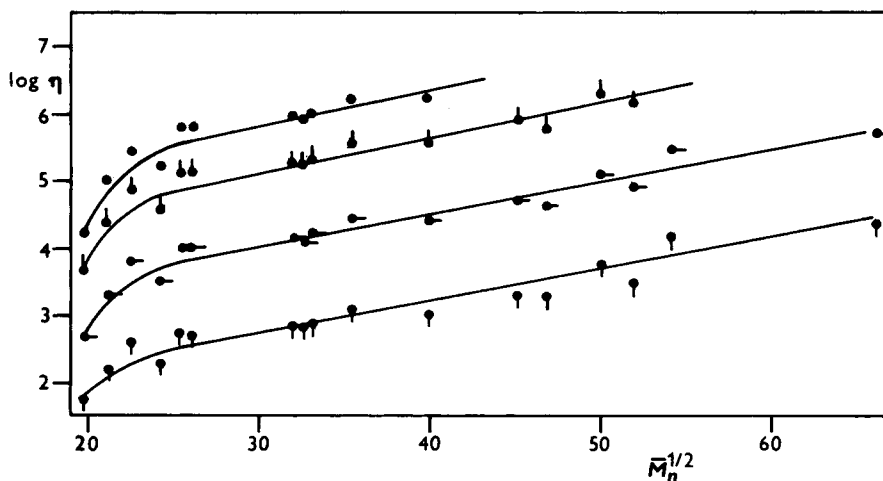


Fig. 2. Dependence of  $\log \eta$  on  $\bar{M}_n^{1/2}$  for unsaturated polyester fractions: (●) 49.6°C; (◐) 60.3°C; (◑) 84.1°C; (◒) 127.0°C.

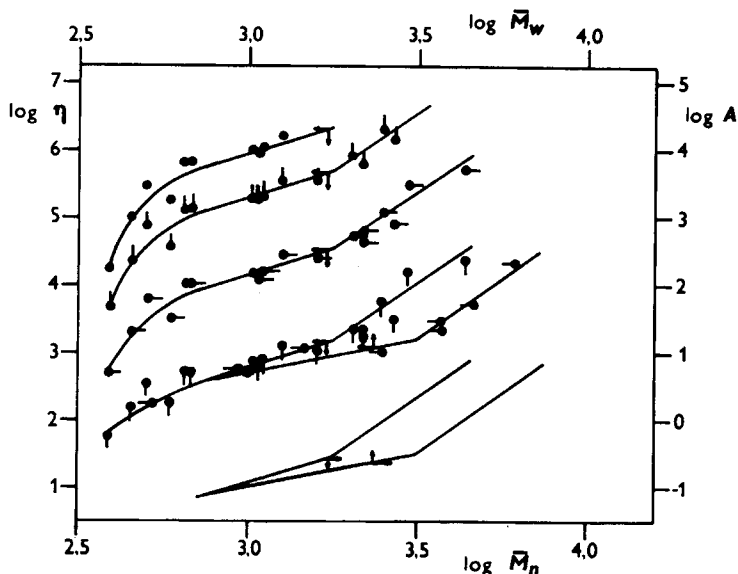


Fig. 3. Dependences of  $\log \eta$  on  $\log \bar{M}_n$  ( $\log \bar{M}_w$ ) and  $\log A$  on  $\log \bar{M}_n$  ( $\log \bar{M}_w$ ) for unsaturated polyester fractions: (●) 49.6°C; (●) 60.3°C; (●—) 84.1°C; (●, —) 127.0°C.

Comparison of the dependences  $\log \eta - \log \bar{M}_n$  with dependence  $\log \eta - \log \bar{M}_w$  shows that  $\bar{M}_{wc}$  is about twice as high as  $\bar{M}_{nc}$  ( $\bar{M}_{nc} \approx 1780$ ,  $\bar{M}_{wc} \approx 3160$ ) and a slope  $a_w$  ( $700 < \bar{M}_w < 3160$ ) is rather lower than  $a_n$  ( $a_n \approx 1.5$ ,  $a_w \approx 1.0$ ). The latter is caused by the fact that the fractions of higher molecular weights are more highly polydisperse than the ones of lower molecular weights.

### The Inherent Friction Factor $\zeta_0$

The dependences of the viscosity  $A$  (mPa·s) at constant friction factor  $\zeta_0$  on molecular weight [ $\log A(\bar{M}_n) - \log \bar{M}_n$  and  $\log A(\bar{M}_w) - \log \bar{M}_w$ ] are shown in Figure 3. The relationship  $\log A(\bar{M}_w) - \log \bar{M}_w$  is given by eq. (9):

$$\log A(\bar{M}_w) = -4 + \log \bar{M}_w \quad (9)$$

which is applicable for  $700 < \bar{M}_w < 3160$ .

The inherent friction factor  $\zeta_0$  was calculated by means of eq. (10):

$$10^{-6} = (N_A/6)(\bar{s}_0^2/M)(1/\nu)(1/M_0)\zeta_0 \quad (10)$$

where  $\bar{s}_0^2/M = 7.33 \times 10^{-18} \text{ cm}^2 \cdot \text{mol} \cdot \text{g}^{-1}$ ,  $\nu(20^\circ\text{C}) = 0.75 \text{ cm}^3 \cdot \text{g}^{-1}$ ,  $M_0 = 25.3$ ,  $\zeta_0 = 2.6 \times 10^{-11} \text{ g} \cdot \text{s}^{-1}$  ( $\log \zeta_0 = -10.6$ ). The determination of  $\bar{s}_0^2/M$  of an unsaturated polyester will be published elsewhere. To calculate the mean molecular weight  $M_0$  of one friction unit ( $ZM_0 = M$ ), we presumed (in accordance with Berry and Fox<sup>2</sup>) that these atoms and groups of atoms were friction units of polyester chain:  $-\text{O}-$ ,  $-\text{CH}_2-$ ,  $-\text{CO}-$ ,  $-\text{CH}=\text{CH}-$ , phenyl, cyclohexyl.

### DISCUSSION

It turned out to be possible to use the free volume concept of the flow to express viscosity-temperature relationship for the unsaturated polyester. Dependences

of  $\log \eta$  on  $1/T$  are not linear over a wider temperature range. Flory<sup>4</sup> reported similar results in viscosity investigations on molten linear saturated polyesters.

Dependences  $\log \eta - \bar{M}_n^{1/2}$  (resp.  $\log \eta - \bar{M}_w^{1/2}$ ) are given for the unsaturated polyester and poly(decamethylene adipate) in Figure 4. The respective straight lines drawn for the unsaturated polyester get rather curved over a low molecular weight range ( $\bar{M}_n < 700$ ). As illustrated in Figure 2, these curves have different courses for various temperatures so that parameters  $\alpha$  and  $T_0$  are not constant. Only above  $\bar{M}_n = 700$  can we consider parameters  $\alpha$  and  $T_0$  to be independent of molecular weight. A further reason for these curvatures could be space differences in dimensions of molecules over low molecular weight range. A certain scatter of experimental values is probably caused by different molecular weight polydispersities of the fractions.

Dependences  $\log \eta - \log \bar{M}_n$  (resp.  $\log \eta - \log \bar{M}_w$ ) are given for the unsaturated polyester and poly(decamethylene adipate) in Figure 5. It is evident that slopes of the respective straight lines have nearly the same values for both polymers. The straight lines drawn for the unsaturated polyester get rather curved over a low molecular weight range for the reasons discussed already above.

Values of  $\bar{M}_{nc}$ ,  $\bar{M}_{wc}$ ,  $Z_{nc}$ , and  $Z_{wc}$  for the unsaturated polyester [resp. poly(decamethylene adipate)] are 1780, 3160, 70, and 125 [resp. 2190, 4470, 138, and 281]. Comparison of values of  $\bar{M}_{wc}$  (resp.  $Z_{wc}$ ) shows that the respective critical values are lower for the unsaturated polyester than for poly(decamethylene adipate). Comparison of the published values<sup>1</sup> of  $Z_{wc}$  determined for linear saturated polyesters ( $Z_{wc} = 200-300$ ) with the ones determined for other polymers ( $Z_{wc} = 500-700$ ) shows that polyesters have relatively low values of  $Z_{wc}$ . The lower values of  $Z_{wc}$  for the more polar polymers (polyesters) are reasonable since the higher forces in this case should result in a higher concentration of chain

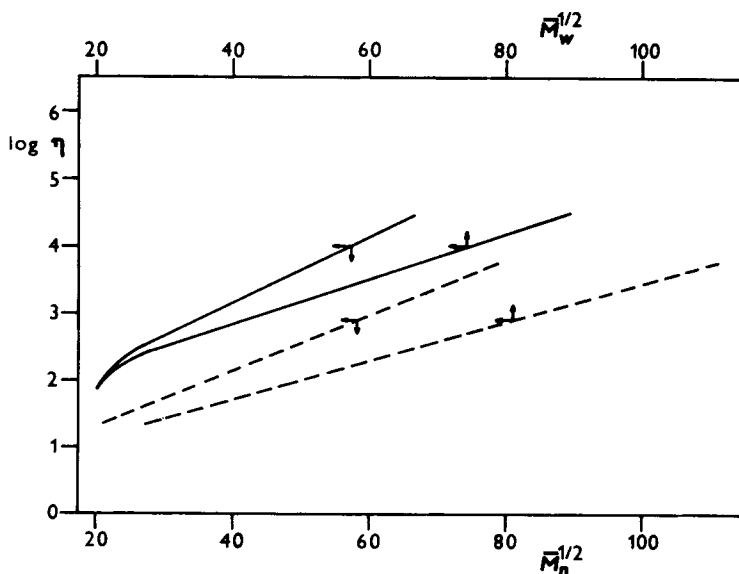


Fig. 4. Dependences of  $\log \eta$  on  $\bar{M}_n^{1/2}$  and  $\log \eta$  on  $\bar{M}_w^{1/2}$ : (—) the unsaturated polyester, 127.0°C; (---) poly(decamethylene adipate), 109.0°C.

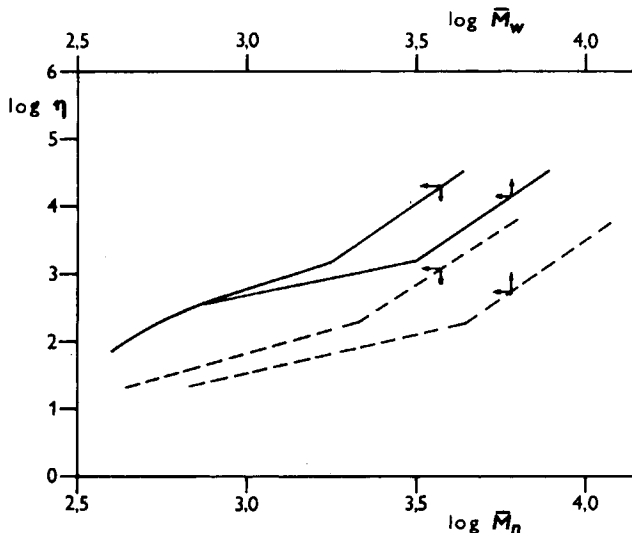


Fig. 5. Dependences of  $\log \eta$  on  $\log \bar{M}_n$  and  $\log \eta$  on  $\log \bar{M}_w$ : (—) the unsaturated polyester, 127.0°C; (---) poly(decamethylene adipate), 109.0°C.

entanglements than in the nonpolar case. Distances between —CO—O— groups within chains of an unsaturated polyester are shorter compared with poly(decamethylene adipate). This may considerably contribute to the lowering of a value of  $Z_{wc}$  of the unsaturated polyester. As well this fact can cause the somewhat higher value of the inherent friction factor  $\zeta_0$  determined for the unsaturated polyester compared with the other polymers<sup>2</sup> ( $-12.5 < \log \zeta_0 < -10.5$ ).

## CONCLUSION

It was found out that it is possible to use the free volume concept of the flow to express viscosity–temperature relationship for the unsaturated polyester. The isothermal viscosity–molecular weight relationship is possible to express by linear dependences  $\log \eta - \bar{M}_n^{1/2}$  ( $\bar{M}_w^{1/2}$ ) or  $\log \eta - \log \bar{M}_n$  ( $\log \bar{M}_w$ ). Parameters  $\alpha$  and  $T_0$  of the Vogel equation seem to be independent of molecular weight above  $\bar{M}_n = 700$ .

Values of  $\bar{M}_{wc}$  (resp.  $Z_{wc}$ ) determined for the unsaturated polyester [3160 (resp. 125)] are markedly lower than those determined for other polymers. The reason of this probably are the high forces between polar groups of the unsaturated polyester chains. This may also cause the somewhat higher value of the inherent friction factor  $\zeta_0$  determined for this polyester ( $\zeta_0 = 2.6 \times 10^{-11} \text{ g}\cdot\text{s}^{-1}$ ).

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