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CALCULATION OF THE WEIGHT AND NUMBER FUNCTIONS OF MOLECULAR WEIGHT DISTRIBUTION FOR OLIGOMERS FROM THE GEL PERMEATION CHROMATOGRAPHY DATA

V. V. EVREINOV, A. K. ROMANOV AND S. G. ENTELIS

Institute of Chemical Physics, Academy of Sciences, Moscow (U.S.S.R.)

SUMMARY

A method is developed to calculate the weight and number functions of molecular weight distribution for oligomers. The influence of the shape of the chromatographic bands of the individual substances on the molecular weight distribution function is discussed, both as the influence on the instrumental spreading and as the change of the refraction index with the molecular weight. The weight, number functions, M_n and M_w were obtained for the condensation oligomers of poly(diethylene glycol adipates) with molecular weight 400-1200.

Gel permeation chromatography (GPC) is a convenient fast method for determining the molecular weight distribution (MWD) of oligomers. However, it is a complicated problem to obtain weight and number MWD functions from the GPC data. TUNG¹ suggested two methods of calculation of the MWD function for polymers: solving the integral equation of a gel chromatogram by the least-squares method, and by the method of "polynomial expansion". These methods, especially in the resolution chromatogram range, are difficult to apply to oligomers. There are practically no literature data on calculations of the MWD function for oligomers.

A method of calculation of the weight and number MWD functions from the GPC data for oligomers has been outlined in the present paper. The influence of shape of the individual substance chromatographic band (SCBIS) and of the changes in instrumental spreading and refraction index with molecular weight on the distribution is discussed.

Let us write the equation of a gel chromatogram $F(v)$, when (SCBIS) is given by a Gaussian function, whose half-width does not depend on eluent volume:

$$F(v) = \sum_{i=1}^n A(v_i) e^{-h(v-v_i)^2} \quad (1)$$

In eqn. 1 v_i is the eluent volume at maximum of Gaussian curve, $A(v_i)$ is a function which characterizes the weight concentration of substance, h is the resolution factor. The interpretation of gel chromatogram $F(v)$ consists in determining the dependence $A(v_i) = f(M_i)$, i.e. in calculating the weight function distribution $w(M)$, if the calibration curve $\log M$ vs. v is known.

was obtained by plotting data from the measurements on HDPE-standards (hydrogenated polybutadiene) (Fig. 2. (+)).

So far no mathematical expression for the relationship between \bar{M} and $[\eta]$ has been found for the LDPE. DROTT¹³, PANARIS AND PRECHNER¹⁸ and CROUZET *et al.*¹⁹ have published viscosity and light scattering measurements on LDPE-fractions, using TCB-solutions at 135° for the viscosity measurements. We have utilised these values to construct a $\log \bar{M}_w$ - $\log [\eta]$ relationship (Fig. 4). From this plot it is possible to obtain $[\eta]$ and subsequently calculate $[\eta] \cdot \bar{M}_w$ for different values of \bar{M}_w .

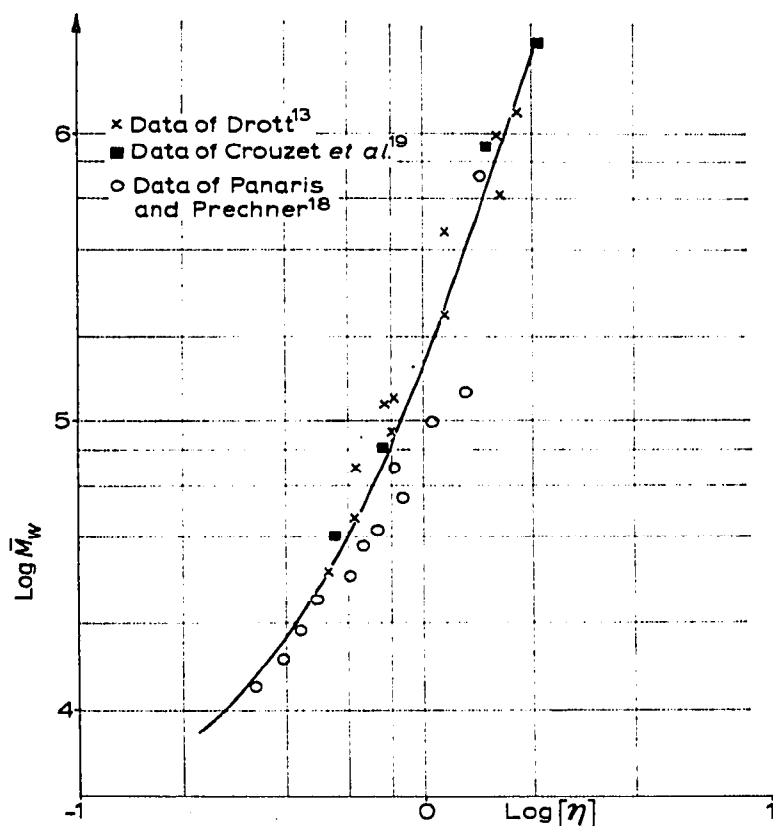


Fig. 4. Relationship between $\log [\eta]$ and $\log \bar{M}_w$ for LDPE.

Using the same calculating procedure as mentioned previously the calibration curve for LDPE (Fig. 2) is obtained *via* the universal calibration curve (Fig. 3). CROUZET *et al.*¹⁹ has published similar calculations starting with data on HDPE and LDPE fractions. The resulting calibration curve for LDPE has the same general appearance and position in relation to the HDPE curve as our LDPE calibration curve.

Treatment of GPC data

Calculation of average molecular weights and plots of weight fraction against $\log M$ (molecular weight distribution (MWD)) from the GPC-curves was carried out by the computer program devised by DROTT AND MENDELSON²¹.

RESULTS AND DISCUSSION

The samples became successively more and more brittle during heat treatment, even at the lowest oxygen levels. The sample treated at the highest temperature, for the longest time in the most oxygen-rich atmosphere acquired a thin brown surface layer. No other sample was discoloured.

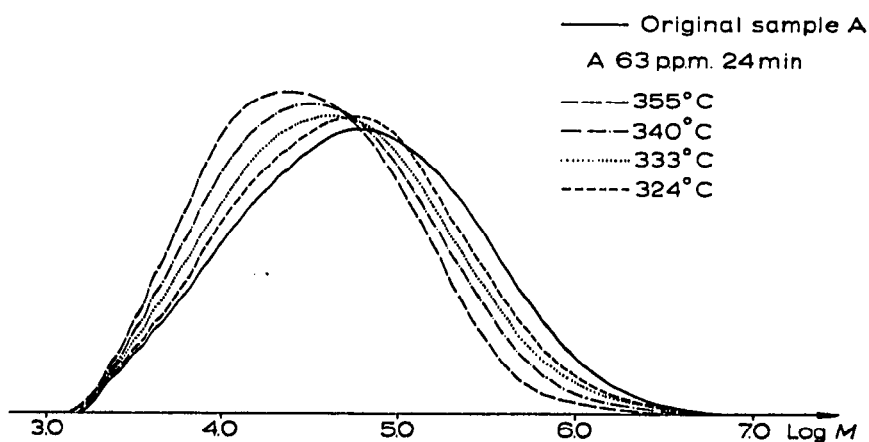


Fig. 5. Weight fraction plotted against $\log M$ (MWD) for sample A, heated for 24 min in 63 p.p.m. oxygen.

None of the samples contained insoluble matter, showing that no (extensive) crosslinking occurred. On the contrary, the heat treatment caused chain scission, clearly demonstrated by a drop in molecular weight (MW), and minor weight losses. The latter effect was followed by TGA-measurements.

In the following paragraphs the effect of temperature, heating time and oxygen content on chain scission is discussed. The experimental work to elucidate time-temperature effects was conducted in 63 p.p.m. oxygen as this low oxygen content gave the same result as oxygen-free nitrogen²².

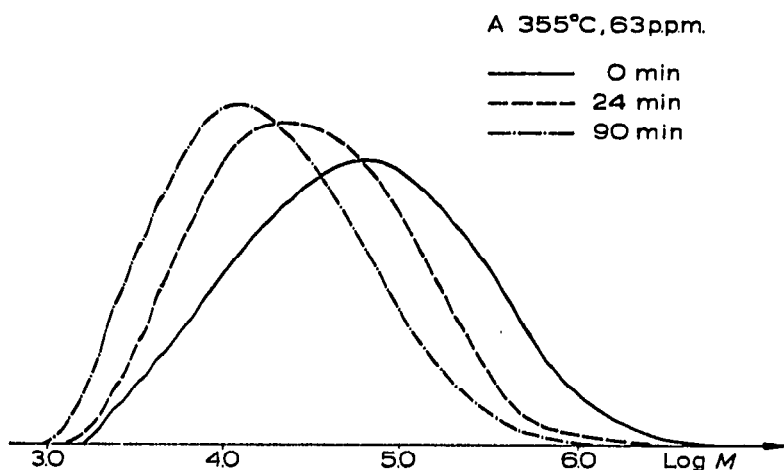


Fig. 6. Weight fraction plotted against $\log M$ (MWD) for sample A, heated at 355° in 63 p.p.m. oxygen.

Effect of temperature and heating time in a nitrogen atmosphere

A series of experiments was conducted in "nitrogen" (63 p.p.m. oxygen). The following time and temperature levels were used (Figs. 5-9 and 13): 2, 6, 12, 24, 90 min; and 284, 315, 324, 333, 340, 355°. Figs. 5 and 6 demonstrate the pronounced effect of temperature and heating time on MWD. The quantity of high molecular weight material diminishes. The highest M -value noticed drops by a factor of two in

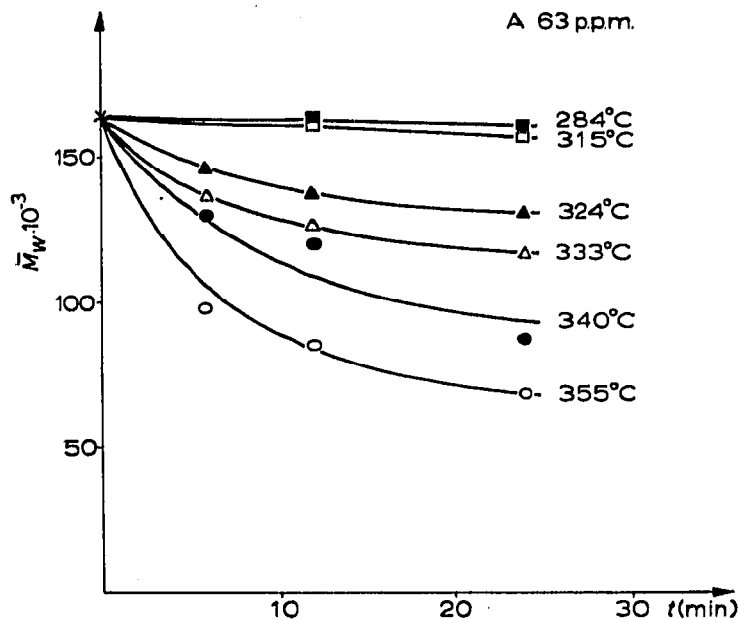


Fig. 7. Change of \bar{M}_w with heating time for sample A heated in 63 p.p.m. oxygen.

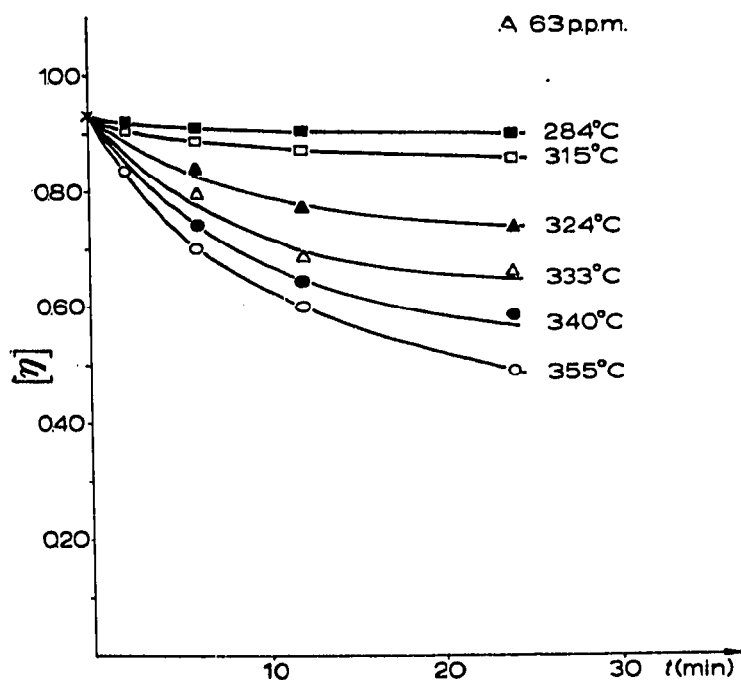


Fig. 8. Change of $[\eta]$ with heating time for sample A heated in 63 p.p.m. oxygen.

each step 0-24-90 min at 355°. However, even after 90 min at 355° material of an M in the order of 10^6 is present.

The low molecular weight end of the MWD is much steeper and does not shift to any appreciable extent up to 24 min at 355°. When the heating time is increased to 90 min, the low molecular weight end drops by a factor of about two. The peak position is moved from $65 \cdot 10^3$ to $12 \cdot 10^3$ and the width of the MWD at 50% peak height is getting smaller.

The TGA-measurements showed the following values:

Time (min)	Temperature (°C)	Weight loss (%)
24	315°	1
24	355°	6
90	355°	17

Fig. 5 shows that a rise in temperature affects the MWD in the same general way as described above for increase in the heating time. The observed changes with time and temperature can be explained qualitatively by the theory of random scission. The high molecular weight end should not vanish completely as the amount of material is small. Thus the MWD is not growing narrower due to the disappearance of the high molecular weight molecules as reported for HDPE¹⁰. According to the random scission

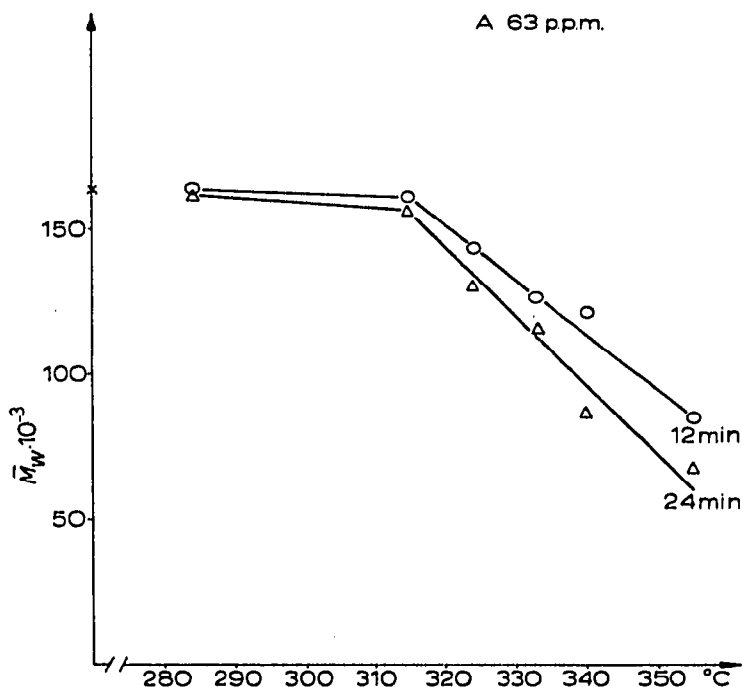


Fig. 9. Change of \bar{M}_w with temperature. Sample A, 63 p.p.m. oxygen.

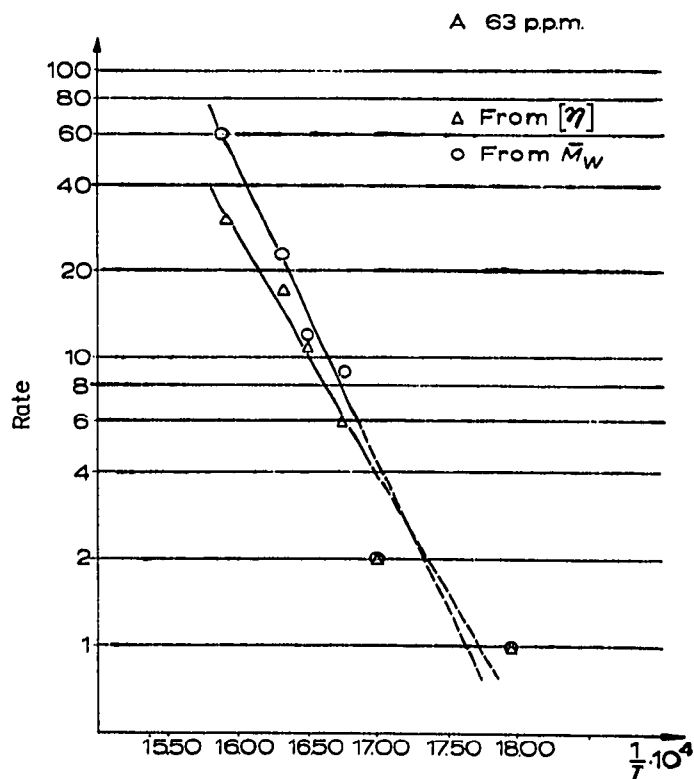


Fig. 10. Arrhenius plot for sample A at 63 p.p.m. oxygen. Data from GPC and viscosity measurements.

theory the main changes will appear in the central part of the MWD, as is observed. The very small changes in the low end and the steepness of the curve is a result of the low statistical probability of bond breaking in a fraction containing small and few molecules.

The fairly large amount of volatile material obtained is not inconsistent with the above reasoning. TSUCHIYA AND SUMI⁷ showed that intramolecular transfer of radicals results in the formation of C_3 , C_2 , C_4 and C_6 fragments mainly. Thus volatile material is not formed mainly from the low molecular weight tail of the MWD, as proposed by QUACKENBOS¹⁰, but from the whole MWD.

For a more quantitative discussion of the degradation process the \bar{M}_w was calculated. It was supplemented with a determination of $[\eta]$, which also afforded the opportunity of comparison with previously published results. The results are given in Figs. 7 and 8, respectively. Hardly any changes in \bar{M}_w or $[\eta]$ are observed at 284 and 315°. At the higher temperatures the curves are characterised by an initial rapid drop, succeeded by a slower change. Such a degradation course is to be expected for LDPE when being subjected to random scission. This is in accordance with previously published data^{1, 10, 11}. To find the threshold temperature, above which changes are fast, the data were rearranged according to Fig. 9. This plot gave a threshold temperature of 315°, which is in close agreement with data reported for HDPE. (TABAR in ref. 10). The decrease in \bar{M}_w on each side of the threshold temperature follows linear relationships. Like QUACKENBOS¹⁰, who worked with HDPE, we have found that the curves in Figs. 7 and 8 may be super-imposed by sliding the time axis. This time scale can be used as a measure of rate. If the rate is unity at 284° we obtain the following values:

Temperature (°C)	Rate ($[\eta]$)	Rate (\bar{M}_w)
284	1	1
315	2	2
324	6	9
333	11	12
340	17	23
355	30	60

These values have been used in the Arrhenius plot (Fig. 10). Activation energies have been calculated from this plot and we found 64 kcal/mole from $[\eta]$ and 69 kcal per mole from \bar{M}_w . These values are in good accordance with the value of 67 ± 5 kcal/mole given by ANDERSON AND FREEMAN⁸ and also with the values of IGARASHI AND KAMBE⁹ who reported 61 and 74 kcal/mole for a LDPE, from TGA measurements. This means that the activation energy is approximately the same for weight loss and MW-decrease in nitrogen as it is in a vacuum for a LDPE resin. According to our previous discussion on the effect of random scission on changes in MWD, this is a further indication that TSUCHIYA AND SUMI's theory⁷ on intramolecular transfer of radicals is valid. The highest probability, by far, is in the medium molecular weight range. Thus the scission of the molecules in this part of the MWD causes both the bulk of the changes in \bar{M}_w and $[\eta]$ as well as the bulk of the formation of volatile material.

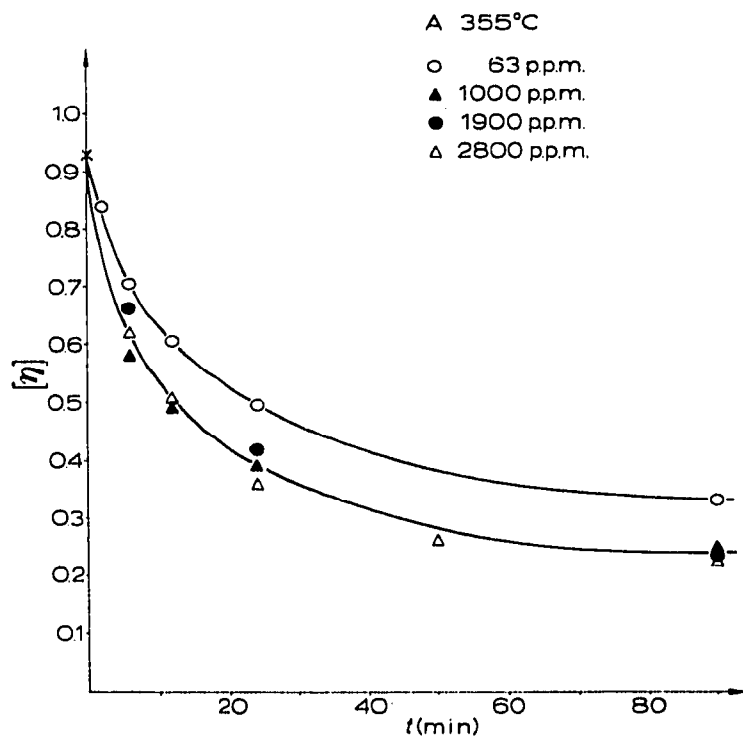


Fig. 11. Change of $[\eta]$ with heating time for sample A heated at 355°

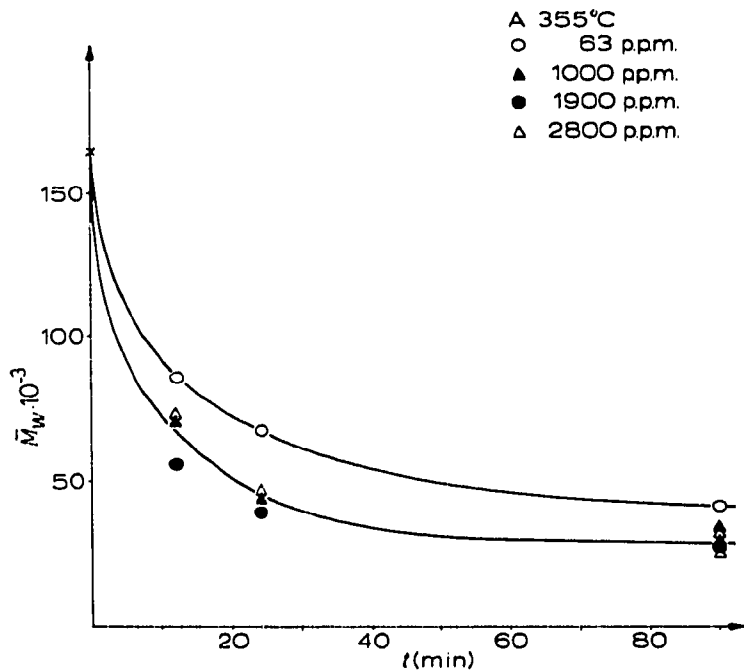


Fig. 12. Change of \bar{M}_w with heating time for sample A heated at 355°.

Effect of oxygen

It is known that the combination of heat and oxygen causes discolouration and formation of odoriferous material while the mechanical and electrical properties of the PE's are declining. In air at temperatures above 250° these changes are very rapid. The present investigation concerns oxygen concentrations below 3000 p.p.m. Changes in MW and MWD will be discussed below, while the changes in chemical structure and crystallinity will be reported elsewhere.

To study the influence of oxygen a series of experiments was conducted at 355°. Heating times were 2, 6, 12, 24 and 90 min and nitrogen containing the following oxygen concentrations was used: 22, 63, 410, 1000, 1900 and 2800 p.p.m. The results are given in Figs. 11-13. Within the range of oxygen concentrations studied an increase in the degradation velocity was observed, but no simple relationship was found. During the investigation we soon found that increasing the oxygen content from 22 to 410 p.p.m. had no effect on the relationship between \bar{M}_w respectively $[\eta]$ and heating time²². Therefore only data from experiments on 63 p.p.m. are given. Furthermore, a similar lack of response was observed on increasing the oxygen content from 1000 to 2800 p.p.m. (Figs. 11 and 12). This means that the experimental results can be summarised in two curves as is shown in Figs. 11 and 12.

The same remarkable tendency was observed when the MWD's were compared with each other. The changes could be summarised in two series covering the two ranges of oxygen concentration (22-410 and 1000-2800 p.p.m.).

Changes in MWD's are shown in Fig. 13. High oxygen content causes a gradually increasing skewness which is pronounced after 90 min. The high molecular weight

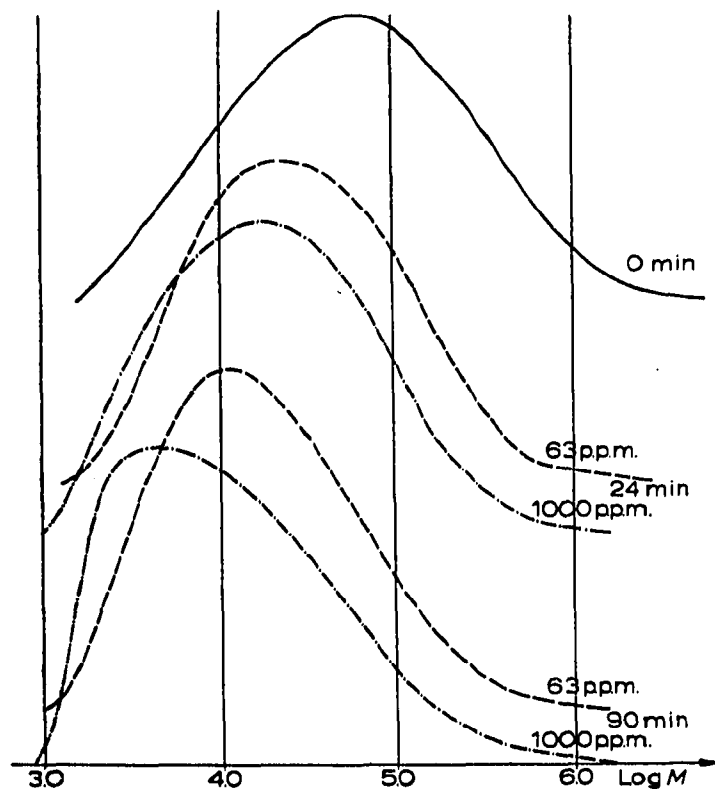


Fig. 13. Weight fraction plotted against $\log M$ (MWD) for sample A heated at 355°.

tail is still in the region of 10^6 and the low end of the MWD remains at about 10^3 . The MWD is very steep at the lower end and the peak position has moved from $\sim 10^4$ to $\sim 5 \cdot 10^3$ ($C_{700}-C_{350}$).

The reason for the difference in degradation rate between low and high oxygen concentrations is not clearly understood. A reaction that involves equilibrium conditions between oxygen and active sites for chain scission in the polymer, could be an explanation. If this is true the oxygen concentration at 410 p.p.m. should be too low for reaction whereas at 1000 p.p.m. reaction occurs. Furthermore at 1000 p.p.m. all active sites ought to be reactive and a further increase in oxygen concentration to 1900 p.p.m. should not cause any further chain scission. Work on elucidating the influence of oxygen on the chain scission is going on in our laboratory.

The curves in Figs. 11 and 12 cannot be super-imposed by sliding the time axis. Therefore it was not possible to construct an Arrhenius plot. The increase in rate at the high oxygen concentrations is 2-4 times, the lower value corresponding to the shortest heating times.

\bar{M}_w/\bar{M}_n and \bar{M}_z/\bar{M}_w values were calculated from GPC data and plotted against heating time at different oxygen levels (Fig. 14).

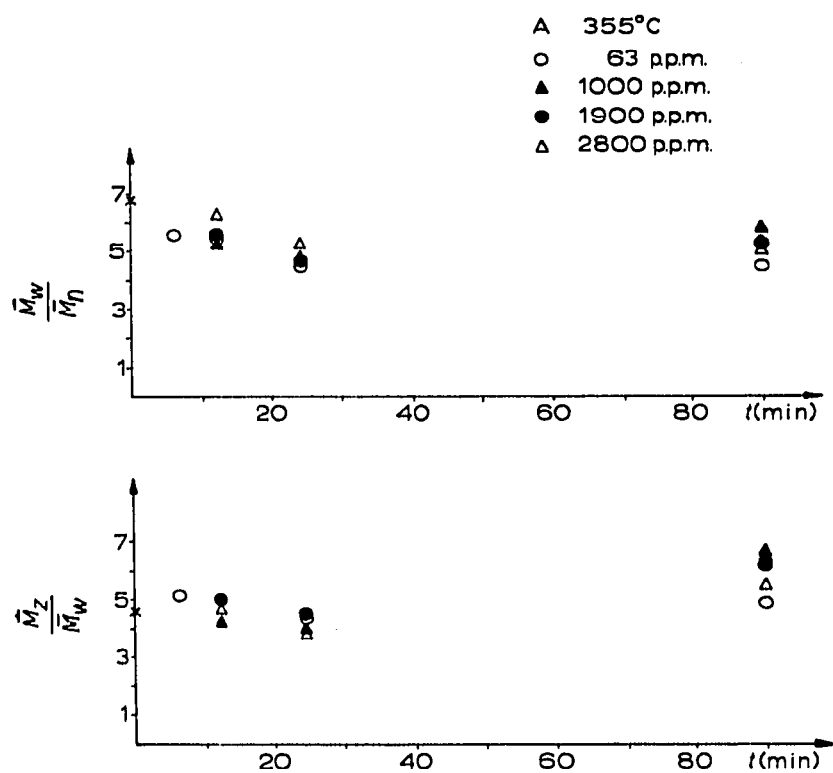


Fig. 14. \bar{M}_w/\bar{M}_n and \bar{M}_z/\bar{M}_w values for sample A, heated at 355°.

The \bar{M}_w/\bar{M}_n and \bar{M}_z/\bar{M}_w values are remarkably constant and not consistent with the drastic drop in \bar{M}_w/\bar{M}_n reported earlier, *e.g.*, by ARNETT AND STACY¹¹, for a HDPE resin. Our plots indicate a shallow minimum in the order of 4 and no continuous decrease of \bar{M}_w/\bar{M}_n approaching a value of 2, which should be expected from current theories of random scission.

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