

Fractionation of Polymers by Liquid-Liquid Distribution

VI. Molecular Weight Frequency Curves for Polyglycols

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The relation between the molecular weight and limiting viscosity number has been determined on unfractionated polyglycol preparations. By means of this relation earlier determined frequency functions of limiting viscosity number have been transformed into molecular weight frequency curves. The accuracy of the curves obtained is discussed.

Molecular weight frequency curves for polymers can be obtained from liquid-liquid countercurrent experiments in which the weights and the molecular weights of the fractions obtained have been determined. The mathematical treatment of the experimental data has been described in Ref.¹ The method for the molecular weight determination must be chosen so that absolute values are obtained for the molecular weights. Such determinations either require relatively large quantities of the samples or are time-consuming and require special techniques. In the experiments reported in the previous papers of this series^{2,3}, it was found that often only small quantities of the samples were obtained in the fractions. For this reason, the present author has chosen to determine the relation between the molecular weight and the limiting viscosity number on unfractionated samples and to then apply this relation to the previously determined curves of frequency *vs.* limiting viscosity number^{2,3}.

We assume that Mark's⁴ modification of the Staudinger relation

$$[\eta] = K \cdot M^x \quad (1)$$

is valid*.

* In connection with work on polyglycols, the relation

$$[\eta] = K \cdot M + l$$

has been used by some other authors. Because the constants in eqn. 1 are sometimes of greater theoretical interest, this mathematical form has been preferred by the present author.

The average molecular weight of the sample can be written

$$\bar{M}^{\alpha} = \int_0^{\infty} M^{\alpha} g([\eta]) d[\eta] \quad (2)$$

where α is fixed by the conditions of the experimental method ⁴ and $g([\eta])$ is the weight frequency function in terms of the limiting viscosity number.

From eqns. 1 and 2, we obtain

$$\frac{1}{\bar{M}^{\alpha}} \cdot \int_0^{\infty} [\eta]^{\alpha/x} \cdot g([\eta]) \cdot d[\eta] = K^{\alpha/x} \quad (3)$$

If \bar{M} is measured for a number of different samples of the polymer with known $g([\eta])$ functions, the left hand side of eqn. 3 can be calculated for different x values. The correct value for x is the one which makes the value of the left hand side independent of the choice of sample.

Such a treatment of the problem has — as far as the author knows — not been performed earlier. The method generally used nowadays is to determine the molecular weight and the limiting viscosity number for fractionated polymer samples and to then regard the fractions as samples containing molecules of only one size. Eqn. 1 is then directly applicable to the experimental $[\eta]$ values. Considering that the polymer samples prepared up to the present are far from homogeneous with respect to molecular weight, this method cannot be regarded as free from objections.

In this investigation, the end group molecular weight of the polyglycol preparations examined has been determined (Table 1). Thus $\alpha = -1$ in the formulae above. In Table 2, the numerical values of the left hand side of eqn. 3 are given for different values of x for the polyglycol preparations reported in Parts IV and V ^{2,3} of this series. As can be seen, it is difficult to estimate the correct x value directly from the table. Because of this, the coefficient of variation ($= v$) has been calculated for the apparent constant at each x value. The magnitude v^2 has been plotted as a function of x . The values of x at which the minimum of this curve occurs is regarded as the correct value. The minimum value was determined under the assumption that the law concerning the rectilinear diameter is valid (Fig. 1). The value found is

Table 1. Number average molecular weights of the polyglycol preparations determined according to the end group method.

Sample	Number of dets.	Number average mol. weight
A 6 000	8	6 600 ± 40
A 4 000	9	3 620 ± 40
A 1 500	10	1 590 ± 30

Table 2. Left member of eqn. 3 calculated for the polyglycol preparations for different values of x .

Sample	Left member of eqn. 3 ($a = -1$)				
	A 1 500	A 4 000	A 4 000	A 6 000	A 6 000
Solvent system	TCW	TAW	TCW	TAW	TCW
$x = 0.5$	21.7	17.3	16.4	11.6	11.6
0.6	45.1	42.1	36.8	33.1	33.6
0.7	74.2	78.9	76.4	69.9	71.1
0.75	95.3	104.1	98.1	89.9	96.7
0.8	113.4	129.9	122.0	125.8	125.7
0.9	150.7	188.3	179.0	189.0	196.1
1.0	195.4	251.3	240.5	278.1	277.4
(∞)	(1 591)	(3 619)	(3 619)	(6 593)	(6 594)

$x = 0.74_5$. The arithmetical mean of the values of $K^{-1/x}$ interpolated from Table 2 was found to be 94.5. The Staudinger relation can thus be written

$$[\eta] = 3.38 \times 10^{-2} M^{0.75} \quad (4)$$

for polyglycol. The range of validity of this relation is difficult to estimate but a lower limit of about $M = 1\ 200$ and an upper limit of about $M = 9\ 000$ seem reasonable.

It is of interest to compare the above constants with those obtained when the calculations were carried out without regard to the width of the frequency curves. The $[\eta]$ values used in these latter calculations were the arithmetical means of the values calculated from the experimental $[\eta]_p$ values for the fractions in the countercurrent experiments. The values of x and K were calculated according to the same principles as above. The v^2 vs. x curve obtained is given in Fig. 1 (dotted curve). The values found were $x = 0.77_4$ and $K = 2.68 \times 10^{-2}$. (The same result is obtained if the method of least squares is applied to the Staudinger relation after taking the logarithm of both sides). The $[\eta]$ versus M curve constructed using these latter x and K values differs only slightly from

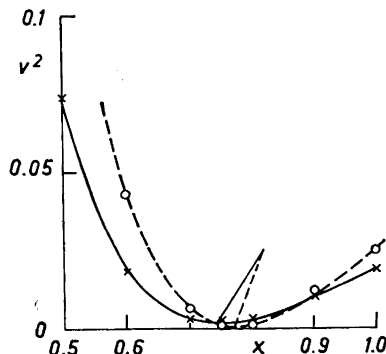


Fig. 1. Graphic determination of the exponent x in eqn. 1 for polyglycols.

the curve obtained from eqn. 4. In the range of validity, the differences amount to 0–3 %. However, the change in K is about 25 %. The experimental data on which the above calculations have been based are too few to permit a penetrating discussion, but the tendency is nevertheless clear.

Eqn. 4 has been used to transform the frequency curves. The results can be seen in Fig. 2. The full-drawn curves are the experimental curves. In the case of polyglycol A 4 000 and A 6 000, the curves from the experiments in the solvent system TCW are the arithmetical means of the curves obtained from the corresponding curves of frequency *vs.* limiting viscosity number. The dotted curves have been calculated using the formula derived by Flory⁵.

The curves obtained with the solvent system TCW are more sharply peaked than those obtained with the solvent system TAW. This effect is more pronounced for polyglycol A 4 000 than for polyglycol A 6 000. The ratio of the resolving powers⁶ of the systems TAW and TCW was calculated to be 1:7.4 in the case of polyglycol A 4 000, the molecules being assumed to have a molecular weight identical to the number average molecular weight of the sample. The curve obtained with the solvent system TCW must therefore be regarded to be the more reliable one. In the case of polyglycol A 6 000, the corresponding ratio was 1:3.0. The differences in the curves obtained are less pronounced than in the case of polyglycol A 4 000. The chief differences appear in the high molecular weight parts of the curves. The double peak of polyglycol A 6 000 could not be detected directly in the experimental $W(p)$ curves obtained in the TAW experiments². This implies that the numerical treatment of the data from the TAW system, as well as the lower resolving power, can influence the results. In the case of polyglycol A 6 000, the results from the solvent system TCW must therefore be regarded as somewhat more reliable.

For polyglycol A 1 500, the resolving power is about 25 times higher in the solvent system TCW than that in the solvent system TAW. In view of the narrowness of the frequency curve, this ratio explains why it was impossible to perform any calculations of the frequency function using data from the TAW experiments.

The ratio of the resolving powers for the experiments with polyglycols A 6 000, A 4 000 and A 1 500 in the solvent system TCW was found to be 1:1.5:2.6. The final frequency curves obtained from data from the solvent system TCW must thus be regarded as nearly equivalent with regard to accuracy although, especially in the experiments with A 6 000, the formation of emulsions interfered considerably.

The agreement between the experimental frequency curves from the TCW experiments and the theoretically calculated frequency curves in Fig. 2 must be regarded as very good. The differences still remaining may be due to errors either in the author's experimental and theoretical treatment of the problem or in the theories of Flory⁵. The latter worker assumes that all steps in the polyreaction in which polyglycol is formed from glycol and ethylene oxide can be characterized by a single rate constant. If one assumes that the first steps of the reaction proceed with a higher velocity than the subsequent steps, then a sharper peaked frequency curve would be obtained. This assumption is only one of the possibilities for explaining the differences. Another

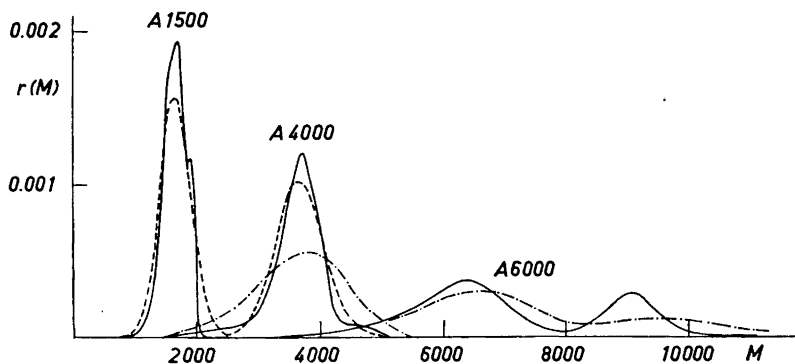


Fig. 2. Molecular weight frequency curves for the three polyglycol preparations investigated. — Curves obtained from the solvent system TCW; - - - Curves obtained from the solvent system TAW; - · - · - Curves according to the theory of Flory.

possible reason for the differences between the calculated and experimental curves in Fig. 2 might be that the frequency curve of the sample is changed by the purification².

In any case, the frequency curves calculated using the theory of Flory are not consistent with the experimental $W(p)$ values if it is assumed that the experimentally obtained relation between limiting viscosity number and partition coefficient is correct. Approximate calculations show that the $W(p)$ values for preparation A 1 500 obtained from the theoretical frequency curve according to Flory⁵, are about 0.010 lower than the experimental values for $8 < p < 11$. This difference must be considered to be far outside the experimental accuracy.

DISCUSSION

The countercurrent distribution of polymers between two immiscible solvents seems to lend itself admirably to the determination of molecular frequency functions. The chief difficulty is to find the two immiscible solvents. This problem will be treated in a forthcoming paper.

From the practical point of view, the method has the advantage over conventional methods that it is completely reproducible and this means that it is not necessary to make any time consuming calculations to decide whether two preparations of the same polymer are equal or not from the molecular frequency point of view. The equilibrium between the two phases is rapidly established, thus making it possible to obtain a large number of fractions in a relatively short time. The sensitivity to temperature is not so great in the investigated cases that an extremely accurate temperature control is required. In a given solvent system, the relation between molecular weight and partition coefficient is fixed. This means that, once this relation is known, only the relative amounts of polymer in each fraction have

to be determined. From these data, the frequency function can be calculated in terms of the partition coefficient and then converted, if required, into the molecular frequency curve. However, for a comparative study, such a recalculation may not be necessary. Sometimes the $\bar{W}(p)$ vs. p curve gives all the information required.

The experimental results of this investigation confirm Flory's theoretical interpretation⁵ of the reaction mechanism for the synthesis of polymers which are formed exclusively by the addition of monomers to a fixed number of polymer molecules.

Except for the highest molecular weight preparation examined in this investigation, the solvent system trichloroethylene-alcohol-water was shown to have a resolving power which was too low compared with the solvent system trichloroethylene-chloroform-water. The former solvent system, however, must not be regarded as useless. If the frequency curve of the polyglycol is broader than that for the preparations used in this investigation, then the system TCW might be unsuitable. Such polyglycol preparations can be obtained, for example, either from mixtures of preparations prepared in the common way or as a condensation polymer synthesized according to the method proposed by Flory⁵. It is then possible that all of the preparation may find its way into the first and last tubes of the countercurrent apparatus. An investigation in the solvent system TAW would, however, in such a case give the desired information.

For polyglycol preparations with molecular weights higher than the ones investigated in this series of articles it seems probable that the solvent system TAW or a solvent system composed of a mixture of trichloroethylene, chloroform, alcohol and water would be most suitable.

EXPERIMENTAL

The number average molecular weights of the polyglycol preparations investigated here were determined by titrimetric end group determinations. A weighed quantity of the preparation was heated under reflux for 1 h with 20 ml 6 % acetic anhydride solution in pyridine on a water bath. After cooling, 15 ml water was added and the refluxing continued for a further 10 min. The remaining liquid was then titrated with 0.5 N KOH in alcohol. A blank titration was carried out on the acetic anhydride-pyridine mixture under the same conditions as those for the sample. Phenolphthalein was used as indicator.

The apparent constants in Table 2 and the molecular weight frequency curves were calculated by means of a Litton digital differential analyzer equipped with graph follower and graph plotter.

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