

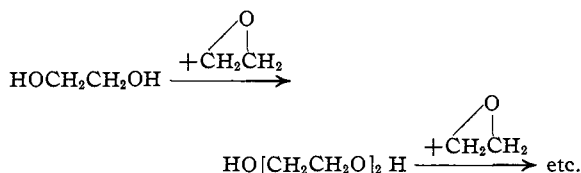
[CONTRIBUTION FROM THE BASIC SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI]

## Molecular Size Distribution in Ethylene Oxide Polymers

BY PAUL J. FLORY

Little progress has been made toward the elucidation of the composition of high polymers by the two known experimental methods, fractionation<sup>1</sup> and ultracentrifugal analysis,<sup>2</sup> both of which yield at best only approximate results. In certain cases, however, it is possible to deduce theoretical relationships by means of which accurate size distributions can be calculated. Such relationships have been presented previously for linear condensation polymers.<sup>3</sup> In this paper size distribution equations will be derived for polymers formed by successive addition of monomers to a fixed number of chains. The bearing of the results on the interpretation of polymer viscosities will be discussed.

It has been known for a long time<sup>4</sup> that ethylene oxide reacts with ethylene glycol to form diethylene glycol and higher glycols by successive additions of ethylene oxide as follows



Ethylene oxide has been found to react similarly with alcohols, amines,<sup>5</sup> mercaptans, and acids, yielding, under proper conditions, polymers of considerable length.<sup>6</sup> In the patent literature there are described many technical processes in which polyoxyethylene glycol chains are built up through the reaction of ethylene oxide with a substance containing an appropriate functional group such as  $\text{NH}_2$ ,  $\text{NH}$ ,  $\text{OH}$ ,  $\text{SH}$  or  $\text{COOH}$ . The available evidence indicates that these processes proceed exclusively by the reaction of monomer (ethylene oxide) with molecules possessing the propagating functional group (*e. g.*,  $\text{OH}$ ); *reaction of polymer with polymer does not occur*. The process can be represented by

(1) G. V. Schulz, *Z. physik. Chem.*, **B30**, 379-399 (1935) has determined the approximate distribution of species in polyisobutylene by fractionation.

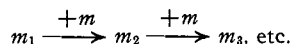
(2) Concerning the use of the ultracentrifuge for determining size distributions, see W. D. Lansing and E. O. Kraemer, *THIS JOURNAL*, **57**, 1369 (1935).

(3) P. J. Flory, *ibid.*, **58**, 1877 (1936).

(4) Wurtz, *Ann. chim.*, (3) **69**, 330 (1863).

(5) H. Hibbert and S. Z. Perry, *Can. J. Research*, **8**, 102 (1933).

(6) H. Staudinger, "Die hochmolekularen organischen Verbindungen," Verlag Julius Springer, Berlin, 1932.



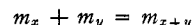
where  $m_1$  is the initial species which bears the propagating functional group,  $m$  represents ethylene oxide, and  $m_x$  is the product formed from  $m_1$  plus  $x - 1$  ethylene oxides.<sup>7</sup>

There are other types of polymers which, under certain conditions, may be formed by analogous mechanisms. It has been suggested that formaldehyde polymerization<sup>8</sup> initiated by traces of moisture proceeds as follows



Similar mechanisms may account for the conversion of cyclic anhydrides,<sup>9</sup> cyclic esters<sup>10</sup> (lactones) and cyclic acetals<sup>11</sup> to the corresponding linear polymers. Some of these reactions are sufficiently reversible to allow interchange to occur, and, as will be shown in another paper, interchange reactions may modify the molecular size distribution.<sup>12</sup>

The distribution of species obtained by the above mechanism of polymerization and the distribution resulting from condensation polymerization are strikingly different. Condensation polymerizations, *e. g.*, the polymerization of a hydroxy acid, proceed by the occurrence of reactions of the type



where  $m_x$  and  $m_y$  represent molecules composed of  $x$  and  $y$  units, respectively,  $x$  and  $y$  being integers from 1 to  $\infty$ . Not only do the polymer molecules react with monomers, but polymers of all sizes react with other polymers. In all of these reactions the same chemical process is involved, and it has been demonstrated in the case of polyesterification that all of them proceed with equal ease.<sup>13</sup>

(7) Perhaps ethylene oxide polymerizes by other mechanisms under some conditions, as for example at high temperature in the absence of suitable propagating functional groups of the sort mentioned above (see ref. 6, p. 289). Only polymers formed by the above mechanism are considered here.

(8) H. Staudinger, ref. 6, p. 255; W. H. Carothers, *Trans. Faraday Soc.*, **32**, 39 (1936).

(9) J. W. Hill, *THIS JOURNAL*, **52**, 4110 (1930); J. W. Hill and W. H. Carothers, *ibid.*, **54**, 1569 (1932); **55**, 5023 (1933).

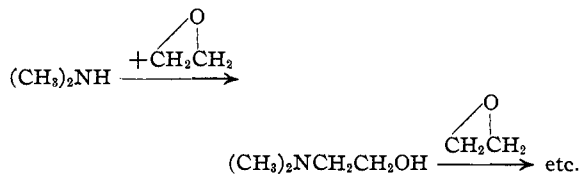
(10) W. H. Carothers, G. L. Dorough and F. J. Van Natta, *ibid.*, **54**, 761 (1932).

(11) J. W. Hill and W. H. Carothers, *ibid.*, **57**, 925 (1935).

(12) P. J. Flory, *ibid.*, **62**, 1064 (1940).

(13) P. J. Flory, *ibid.*, **61**, 3334 (1939).

The treatment presented below is applicable to polymerization processes which fulfill the following two conditions: (i) the total number of molecules possessing propagating functional groups (*e. g.*, the total number of glycol molecules) must remain constant throughout the reaction; (ii) the chains must be built up by a sequence of kinetically identical additions of monomer (ethylene oxide). In cases where the initial propagating molecules are neither glycols nor alcohols, *e. g.*, in the process<sup>6</sup>



condition (ii) will not be entirely satisfied. The rate of the first step will in general differ from the rates of subsequent steps, although the rates of the latter should not differ appreciably from one another. If the reaction is carried out under conditions such that reaction of the initial propagating molecules (*e. g.*,  $(\text{CH}_3)_2\text{NH}$  above) with ethylene oxide is substantially complete before more than a small fraction of the ethylene oxide has been consumed, then the following treatment will serve as a satisfactory approximation. The first addition product ( $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$ , above) must then be considered the initial chain propagator. In cases where the initial step is extremely slow, the treatment of Dostal and Mark<sup>14</sup> may be approximately applicable.

The fundamental equations may be derived as follows. Letting  $N_1, N_2, N_3$ , etc., be the numbers of the species  $m_1, m_2, m_3$ , etc., which possess zero, one, two, etc., added ethylene oxides

$$dN_1/dt = -fN_1 \quad (1)$$

where  $f$  is some function dependent upon the kinetics of the process and the manner in which it is carried out. Presumably,  $f$  (which includes the velocity constant) will be a function of the ethylene oxide concentration, but it may be a function of other variables also, such as  $t$  and the number of propagating molecules  $N^0$ . The solution of the present problem depends in no way upon the nature of  $f$ , so long as it is consistent with the above conditions. In view of condition (ii), the rate at which  $m_2$  is converted into  $m_3$  must be, similarly,  $fN_2$ . Hence

$$\begin{array}{l}
 dN_2/dt = fN_1 - fN_2 \\
 dN_3/dt = fN_2 - fN_3
 \end{array} \quad (2)$$

(14) H. Dostal and H. Mark, *Z. physik. Chem.*, **B29**, 299 (1935).

The rate of disappearance of ethylene oxide is

$$-dm/dt = fN^0 \quad (3)$$

The ratio at time  $t$  of ethylene oxide consumed to  $N^0$  is given by

$$\nu = \Delta m/N^0 = \int_0^t f dt \quad (4)$$

Also

$$d\nu = f dt \quad (4')$$

Substituting (4') in (1) and (2)

$$dN_1 = -N_1 d\nu \quad (5)$$

$$dN_x = (N_{x-1} - N_x) d\nu \quad (6)$$

Integrating (5)

$$N_1 = N^0 e^{-\nu}$$

Substituting this equation in (6) when  $x = 2$  and integrating the resulting differential equation

$$N_2 = N^0 \nu e^{-\nu}$$

Substituting this equation in (6) with  $x = 3$  and integrating

$$N_3 = N^0 (\nu^2/2) e^{-\nu}$$

It is evident that continuation of this process yields

$$N_x/N^0 = e^{-\nu} \nu^{x-1} / (x-1)! \quad (7)$$

This general expression (7) for the mole fraction of  $x$ -mer in the polymer (exclusive of unreacted ethylene oxide) is Poisson's distribution formula. From the nature of the problem dealt with here, it is obvious, without the above derivation, that the numbers of molecules of various sizes must be represented by Poisson's distribution.<sup>15</sup> A brief kinetic derivation has been included in order to point out the scope of applicability of (7) to size distribution problems.

The weight fraction distribution is usually of more interest than the mole fraction distribution. Since the molecular weight of the  $x$ -mer species is given by

$$M_x = xM + (M^0 - M)$$

where  $M$  is the molecular weight of one unit (ethylene oxide) and  $M^0$  is the molecular weight of the initial molecule (*e. g.*, ethylene glycol) from which growth proceeded, the weight fraction of  $x$ -mer is

$$\begin{aligned}
 w_x &= \frac{M_x N_x}{(\nu M + M^0) N^0} = \\
 &= \left[ \frac{x + (M^0 - M)/M}{\nu + M^0/M} \right] e^{-\nu} \nu^{x-1} / (x-1)! \quad (8)
 \end{aligned}$$

The subsequent discussion will deal with the case in which  $M^0 = M$ . Hence

$$w_x = [\nu/(\nu+1)] e^{-\nu} \nu^{x-2} / (x-1)! \quad (9)$$

(15) See T. C. Fry, "Probability and its Engineering Applications," D. Van Nostrand Co., New York, N. Y., 1928.

Even when  $M^0 \neq M$ , (9) may be used for high polymers without significant error.

The number average molecular weight,<sup>16</sup> which equals the total weight of polymer in molecular weight units divided by the number of molecules, is given by

$$M_n = \nu M + M^0 \quad (10)$$

or, when  $M^0 = M$

$$M_n = M(\nu + 1) \quad (10')$$

The degree of polymerization, *i. e.*, the *number average* value of  $x$ , is given by

$$DP = \nu + 1 \quad (11)$$

For condensation polymers the weight fraction distribution is given by<sup>17</sup>

$$w_x = (1 - p)^2 x p^{x-1} \quad (12)$$

where  $p$  is the fraction of the functional groups which have undergone condensation. Their degree of polymerization is given by

$$DP = 1/(1 - p) \quad (13)$$

The solid curves in Figs. 1 and 2 represent weight fraction distributions, calculated from (9), for polyethylene oxides (or other polymers formed by reactions conforming with (i) and (ii)). The values of  $\nu$  are included with each curve. For comparison, portions of two condensation polymer distributions have been included also (broken curves). The one shown in Fig. 1 has been calculated from (12) when  $p = 0.9091$ .

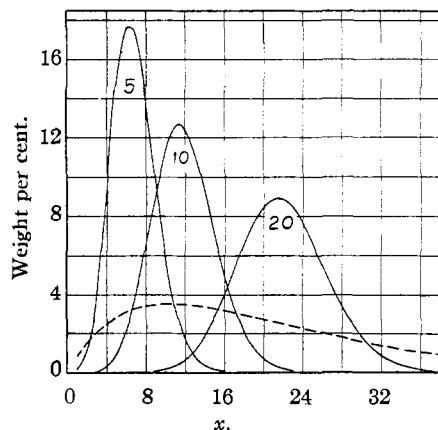


Fig. 1.—Weight per cent. vs. number of units for  $\nu = 5$ , 10 and 20. The broken curve represents a  $DP = 11$  condensation polymer.

(16) The terms *number average* and *weight average* and their definitions were introduced by E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935). The number average molecular weight, defined by  $M_n = (1/N^0) \sum N_x M_x$ , is the average obtained by end-group, osmotic, ebullioscopic or cryoscopic methods. The weight average is defined by equation (14), *cf. seq.*

(17) The symbol  $w_x$  is used here in place of the  $\Pi_x$  of an earlier paper, *ref. (3)*.

This curve and the  $\nu = 10$  polyethylene oxide curve possess the same number average, *i. e.*,  $DP = 11$  for each. Both the  $\nu = 100$  curve and the broken curve in Fig. 2 represent  $DP = 101$ .

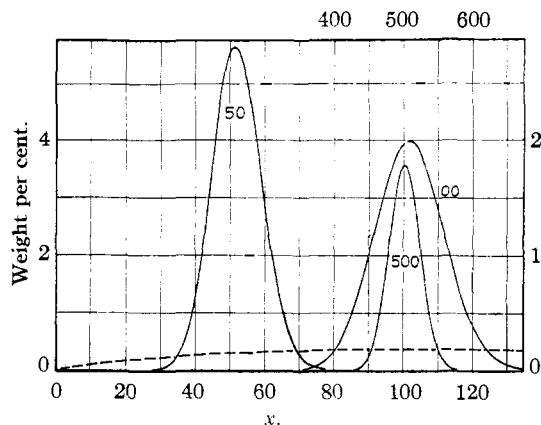


Fig. 2.—Weight per cent. vs. number of units for  $\nu = 50$ , 100 and 500. The broken curve represents a  $DP = 101$  condensation polymer. The  $\nu = 500$  curve is drawn to the scales along the upper and right margins; scales for the other curves are given along the lower and left margins.

The much greater homogeneity of the polyethylene oxide distribution compared with the condensation polymer distribution is apparent in these graphs. For example, in the range  $x = 8-16$ , inclusive, there is included 79.6% of the  $DP = 11$  ( $\nu = 10$ ) polyethylene oxide; only 27.3% of the  $DP = 11$  condensation polymer lies in the same range of sizes. The weight percentages of monomer in these two polymers are 0.041 (exclusive of unreacted ethylene oxide) and 0.826, respectively. At  $DP = 101$  (Fig. 2) the difference is even more pronounced: in the range 90-112, inclusive, one finds 74.8% of the polyethylene oxide, but only 8.35% of the condensation polymer; the calculated weight percentages of monomer are  $4 \times 10^{-42}$  and  $10^{-2}$ , respectively.

The other feature of the polyethylene oxide distribution which should be mentioned is the dependence of the heterogeneity on  $\nu$ . Suppose the breadth of the curve midway between the maximum and the  $x$ -axis be adopted as the measure of heterogeneity. The number of species included in such a range increases as  $\nu$  increases. However, the ratio of this breadth to  $\nu + 1$ , the distance of the maximum from the ordinate axis, decreases as  $\nu$  increases. From this point of view the *relative* heterogeneity decreases as  $\nu$  increases. Comparison of the  $\nu = 100$  and 500 curves in Fig. 2 demonstrates this feature.

Kraemer and Lansing<sup>16</sup> have called attention to the necessity of using the weight average molecular weight  $M_w$ , defined by

$$M_w = \sum w_x M_x \quad (14)$$

in the Staudinger relationship between the viscosity of a dilute solution of a polymer and its molecular weight. Recently the author<sup>18</sup> has found that the weight average molecular weight of linear polyesters can be expressed as a simple function of their viscosity in the liquid state. Whereas molecular weight determinations by cryoscopic, osmotic, and end-group methods yield number averages, viscosity methods yield weight averages when applied to heterogeneous polymers. It is important, therefore, to know the relationship between these two averages for a given distribution.

Substituting (9) in (14) and placing  $M_x = xM$

$$M_w = M \left( \frac{\nu e^{-\nu}}{\nu + 1} \right) \sum_1^{\infty} \frac{x^2 \nu^{x-2}}{(x-1)!} \quad (15)$$

The summation rearranges to

$$\begin{aligned} & \sum_2^{\infty} \frac{(x^2 - 1)\nu^{x-2}}{(x-1)!} + \sum_1^{\infty} \frac{\nu^{x-2}}{(x-1)!} \\ &= \sum_3^{\infty} \frac{\nu^{x-2}}{(x-3)!} + 3 \sum_2^{\infty} \frac{\nu^{x-2}}{(x-2)!} + \sum_1^{\infty} \frac{\nu^{x-2}}{(x-1)!} \\ &= (\nu + 3 + 1/\nu) \sum_0^{\infty} \nu^x / x! \\ &= (\nu + 3 + 1/\nu)e^{\nu} \end{aligned}$$

Substituting this expression for the summation in (15)

$$M_w = M(\nu^2 + 3\nu + 1)/(\nu + 1) \quad (16)$$

Dividing (16) by (10')

$$M_w/M_n = 1 + \nu/(\nu + 1)^2 \quad (17)$$

This ratio of weight average to number average is plotted as a function of  $DP$  in Fig. 3 (lower

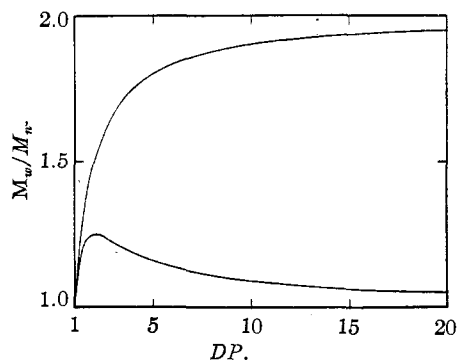


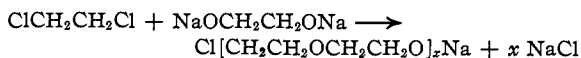
Fig. 3.—Ratio of weight average to number average as a function of  $DP$ . Upper curve, condensation polymers; lower curve, polyethylene oxides.

(18) P. J. Flory, *THIS JOURNAL*, **62**, 1057 (1940).

curve). The ratio approaches unity asymptotically as  $\nu$  increases. For condensation polymers this ratio, which has been shown<sup>3</sup> to be equal to  $1 + p$ , approaches two as a limit with increasing  $DP$  (upper curve in Fig. 3).

The ratio  $M_w/M_n$  may be regarded as a measure of the non-uniformity of the size distribution,<sup>2</sup> a value of unity representing complete homogeneity. On this basis polyethylene oxide heterogeneity must disappear as the average molecular weight becomes infinite. This does not mean that an extremely high molecular weight polymer would be composed essentially of a single species. Rather, it is the *relative* heterogeneity discussed above which disappears as the molecular weight becomes indefinitely large. However, when a high molecular weight polyethylene oxide is subjected to the types of experiments frequently applied to polymeric substances, *e. g.*, to viscosity measurements, ultracentrifugal analysis, and diffusion experiments, it may be expected to behave essentially as if it were a single species. This is in sharp contrast to condensation polymers which approach a constant degree of non-uniformity ( $M_w/M_n$ ) as the average molecular weight approaches infinity.

Hibbert and co-workers<sup>19</sup> have prepared polyoxyethylene glycols by the reaction of the dihalide of a lower polyoxyethylene glycol with the mono-sodium alcoholate of another polyoxyethylene glycol. The polymers so prepared have been shown to be structurally identical<sup>20</sup> with polyethylene oxides. It should be possible to prepare heterogeneous polyoxyethylene glycols by the reaction



which, being a condensation polymerization, should yield the typical condensation polymer distribution. After conversion of the end-groups to OH, the polymer should be identical, except in size distribution, with a polymer prepared from ethylene oxide and a small amount of ethylene glycol under conditions such that (i) and (ii) above are fulfilled. Comparison of their number average and weight average molecular weights, the latter determined viscometrically, would provide an experimental test of the size distribution equations.

(19) S. Z. Perry and H. Hibbert, *Can. J. Research*, **B14**, 77 (1936); R. Fordyce, E. L. Lovell and H. Hibbert, *THIS JOURNAL*, **61**, 1905 (1939).

(20) W. Barnes and S. Ross, *ibid.*, **58**, 1129 (1936).

### Summary

It has been shown that in a polymer formed exclusively by the addition of monomers to a fixed number of polymer molecules, the numbers of species of various sizes are represented by Poisson's distribution law. Equations representing weight fraction distributions have been derived, and the calculated weight per cents. of various species in several polymers having average sizes of 6 to 500 units are shown graphically.

The distribution for these polymers, typified by the polyethylene oxides, has been contrasted with the distribution in condensation polymers. The former are much more homogeneous. Whereas the ratio of weight average to the number average molecular weight of condensation polymers approaches two as the degree of polymerization increases, for the polyethylene oxide distribution this ratio approaches unity.

CINCINNATI, OHIO

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## The Nature of the Thiocyanate Complex of Molybdenum

By C. F. HISKEY\* AND V. W. MELOCHE

In the determination of small amounts of molybdenum, the molybdenum as molybdate is reduced with stannous chloride in the presence of an alkali thiocyanate. The red coloration which is formed under these circumstances, is used in a wide variety of colorimetric procedures.<sup>1</sup> The earliest observations of this reaction were made concurrently by Braun and by Skey.<sup>2</sup> About forty years later, Chilesotti<sup>3</sup> electrolyzed acid solutions of molybdates from which he presumably obtained trivalent molybdenum. He reported that when these solutions were treated with potassium chloride or potassium thiocyanate, red salts were formed with a composition of  $K_3Mo(SCN)_6 \cdot 4H_2O$  and  $K_3MoCl_6$ . Somewhat later Sand<sup>4</sup> and Rosenheim<sup>5</sup> carried out detailed investigations of the complexes which molybdenum formed in the trivalent and pentavalent states. They performed their reductions electrolytically, treating the solutions with an alkali thiocyanate and then extracting the red colored forms with ether. From the ethereal extracts complexes were precipitated with pyridine or quinoline, and, from an analysis of the complexes, these workers attempted to deduce its structure. The complex was variously reported at that time as  $MoO(SCN)_3$ ,  $Mo(OH)_2(SCN)_3$  and as  $R_2MoO-$

$(SCN)_3$  where the R was an alkali atom. In addition to these structures they also were successful in isolating other series of thiocyanate complexes which were formed under nearly identical conditions. In some of these structures the molybdenum was trivalent and the complexes possessed different degrees of hydration. Other compounds differed only in the amount of alkali chloride bound into this complex. In view of the wide variety of structures observed, it becomes extremely difficult to decide which of these formulas should be assigned to the compound under question. Barbieri considered the thiocyanate complex to be  $MoO(SCN)_3 \cdot H_2O$ . In 1926, Krauskopf and Schwartz<sup>6</sup> reported  $Mo(SCN)_3$  on the basis of a simple analysis of the ether extract. However, Wm. Wardlaw and his students<sup>7</sup> reinvestigated the problem of the thiocyanate complex formation and, as a result of a number of experiments decided that the structure of the complex could be either  $(H_2MoO_2(SCN)_3)$  or  $H_2(MoO(SCN)_3)$  although he also isolated a large number of different salts series of the type  $H_2-(Mo_2O_3(SCN)_6)$ . Thus, again no positive identification of the desired structure could be made.

In considering these variously proposed structures, it seemed somewhat doubtful to us that one could assume that the compounds isolated from the dark colored oily mixtures which these workers obtained were identical with the red thiocyanate used in the analytical determination of molybdenum. In view of the more drastic conditions

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(1) Kedesdy, *Mitt. kgl. Materialprüfungsamt*, **31**, 173 (1913); Maag and McCollam, *Ind. Eng. Chem.*, **17**, 524 (1925); James, *Ind. & Eng. Chem., Anal. Ed.*, **4**, 89 (1932); Hurd and Allen, *ibid.*, **7**, 396 (1935).

(2) Braun, *Z. anal. Chem.*, **6**, 86 (1867); Skey, *Chem. News, Am. Reprint*, **1**, 296 (1867).

(3) Chilesotti, *Atti. accad. Lincei*, **12**, ii, 22, 67 (1903).

(4) Sand and Burger, *Ber.*, **38**, 3384 (1905); also Maas and Sand, *ibid.*, **41**, 1500, 1861, 3367 (1908); **42**, 2642 (1909).

(5) Rosenheim and Koss, *Z. anorg. Chem.*, **49**, 148 (1906).

(6) Krauskopf and Schwartz, *This Journal*, **48**, 3021 (1926).

(7) James and Wardlaw, *J. Chem. Soc.*, 2726-2739 (1928).