Molecular Weight Distribution and Polymerization Kinetics in Some New Catalytic Processes

C. Mussa I.V.

Montecatini S.p.A. and Istituto Chimico dell'Università di Torino, Italy

I. INTRODUCTION

The purpose of the present work is to suggest an interpretation of the most outstanding features of the molecular weight (MW) distributions observed in low pressure polyethylene (LPP).[1-8]

Such interpretation is based on a number of assumptions; the first of which is that the general scheme of the polymerization mechanism proposed by Natta and co-workers[9-19] for stereospecific polymerization, particularly of propylene, can be accepted also in the case of the LPP.

It is observed, in this connection, that this polymerization mechanism has been already correlated (e.g., see refs. 9,20–22) to Ziegler's catalyst system and to its performance in the case of polyethylene. Furthermore, it has been observed by Natta and co-workers[16] that the polymerization mechanisms of different stereoisomeric fractions seem to be similar, from a kinetic point of view, independent of their steric features. Finally, it appears[19,23] that isotactic polypropylene also has a broad MW distribution.

II. OUTSTANDING FEATURES OF THE MW DISTRIBUTION OF LPP

Feature A

In the majority of the LPP samples examined until now, the experimental points representing the cumulative weight distribution (CWD) as a function of the degrees of polymerization (DP) *tend* towards a straight-line alignment in a particular coordinate system. In this coordinate system, the cumulative weight fractions are plotted in a probability scale (calculated by means of the normal error function) and the DP (which in the following formulas are indicated by x) are plotted in a logarithmic scale. Such a coordinate system, namely a probability chart having a logarithmic scale, will be called here: "prob-log plot." It is evident that straight-line graphs are also obtained when the CWD are given, instead of as a function of x, as a function of any measurable quantity y satisfying the following conditions: (*a*) It is a limit value for zero interaction of the macromolecules with each other (e.g., for zero concentration, if y is a solution property). (*b*) It is related to the DP by a relationship such as

$$y = Kx^\alpha \qquad (1)$$

In most practical instances y is the intrinsic viscosity or the inherent viscosity. But other measurable quantities, such as the sedimentation constant or the translational diffusion coefficient, may be convenient for the investigation of MW distribution.[24]

The fact that the MW distribution has often been found to be "broad" will not be considered the most important feature here, but merely as a particular case of Feature A occurring when, in the prob-log plot, the slope of the straight-line graph on the probabilistic axis is steep. This is also true for the feature, particularly stressed by other authors, that unusually high percentages of very low MW species are often present in the polymers considered here. In the writer's opinion the fundamental feature is the more general analytical one which has been termed "Feature A." This feature becomes more evident and can be subjected to more reliable experimental control when the MW distribution is "broad." But, in principle, broad as well as narrow MW distributions can be expected when Feature A is verified.

The following differential weight distribution (DWD) formula is now suggested as a general DWD formula which satisfies the condition of being in agreement with Feature A:

$$w(x)dx = Ax^n \exp\left\{-\left(\frac{1}{\gamma}\ln\frac{x}{x_0}\right)^2\right\} dx \qquad (2)$$

where n, x_0, γ, are distribution parameters, and A is a normalization factor. Under the usual normalization condition

$$\int_0^\infty w(x)dx = 1 \qquad (3)$$

we get

$$A = \frac{\exp\left\{-\left(\frac{n+1}{2}\,\gamma\right)^2\right\}}{\gamma(\pi)^{1/2}\,x_0^{(n+1)}} \qquad (4)$$

It is immediately seen that by introducing the auxiliary variable:

$$t = [(2)^{1/2}/\gamma]\,(\ln\,(x/x_0) - [(n+1)/2]\gamma^2) \qquad (5)$$

eq. (2) becomes

$$w(t)dt = [1/(2\,\pi)^{1/2}]\exp\left\{-t^2/2\right\}dt \qquad (6)$$

which is the normal error function. Since the auxiliary variable t is a linear function of $\ln x$, it follows that the CWD obtained from eq. (2) can be represented by straight lines in a prob-log chart.

The advantages of using straight line plots of the experimental CWD data have been already illustrated.[1, 3, 5, 7, 25-28] The practical rules already given[5] can be readily extended to the generalized DWD eq. (2). In subsequent work a detailed analysis of experimental data by means of this kind of plot will be given; for now the following can be stated: (1) the slope s of the straight-line graphs on the probabilistic axis ($x = 0$ or $y = 0$) is given by

$$s = \gamma/(2)^{1/2} \qquad (7)$$

or

$$s' = \alpha\gamma/(2)^{1/2} \qquad (7')$$

depending on whether the CWD data are given as a function of x or as a function of y. (2) The intersection of the straight-line graph with the logarithmic axis ($t = 0$) is located at a value $c = x_{1/2}$ (or $y = y_{1/2}$) corresponding, as is seen from eq. (6), to the 50% ordinate of the CWD curve; this value, from eq. (6), is given by

$$x_{1/2} = x_0 \exp\left\{[(n+1)/2]\,\gamma^2\right\} \qquad (8)$$

or

$$y_{1/2} = y_0 \exp\left\{[(n+1)/2]\alpha\gamma^2\right\} \qquad (8')$$

where $y_0 = Kx_0^\alpha$.

Equations (7) through (8') show that the straight-line graphs allow the direct determination of only one of the distribution parameters: γ or

$\alpha\gamma$. As far as x_0 (or y_0) and n are concerned, only a relationship between them is obtained, such as in eq. (8) or eq. (8'). Hence it is possible to attribute an arbitrary x value to n and a corresponding x_0 (or y_0) value can be calculated. Besides, it is a general analytical fact that a straight line can define only two independent parameters.

Thus it is seen that in the case of a MW distribution corresponding to eq. (2) any property depending only on the DP distribution itself and on a function of the DP such as eq. (1) cannot independently determine n and x_0.

This last statement is confirmed by the following formulas deduced from eqs. (2) through (8'); these formulas, according to the writer's experience, may also be of some practical use in the evaluation of experimental data concerning polymers which are supposed to have a MW distribution of the type in eq. (2).

The DP corresponding to the maximum of the differential distribution by weight (given as a function of the DP) is

$$x_m = x_0 \exp\left\{n\gamma^2/2\right\} = x_{1/2}\exp\left\{-s^2\right\} \qquad (9)$$

The DP corresponding to the maximum of the differential distribution by number (as a function of the DPs), or the "most probable" DP, as defined in ref. 28, is

$$x_p = x_0 \exp\left\{[(n-1)/2]\,\gamma^2\right\}$$
$$= x_{1/2}\exp\left\{-2s^2\right\} \qquad (10)$$

The corresponding maxima of the same differential distributions, when they are given as functions of the variable t are

$$x_m' = x_0 \exp\left\{[(n+1)/2]\,\gamma^2\right\} = x_{1/2} \qquad (9')$$

and

$$x_p' = x_0 \exp\left\{(n/2)\,\gamma^2\right\} = x_{1/2}\exp\left\{-s^2\right\} \qquad (10')$$

The number-average DP is

$$x_n = x_0 \exp\left\{(2n+1)\,(\gamma^2/4)\right\}$$
$$= x_{1/2}\exp\left\{-s^2/2\right\} \qquad (11)$$

The weight-average DP is

$$x_w = x_0 \exp\left\{(2n+3)\,(\gamma^2/4)\right\}$$
$$= x_{1/2}\exp\left\{s^2/2\right\} \qquad (12)$$

The z-average DP is

$$x_z = x_0 \exp\left\{(2n+5)\,(\gamma^2/4)\right\}$$
$$= x_{1/2}\exp\left\{3s^2/2\right\} \qquad (13)$$

Their ratios (or the "unhomogeneity ratios") are

$$x_w/x_n = x_z/x_w = \exp\{\gamma^2/2\} = \exp\{s^2\} \quad (14)$$

(hence such ratios depend only on the parameter γ).

If y_m is the average value of the quantity y measured for the whole polymer sample,

$$y_m = y_0 \exp\{(\alpha\gamma^2/4)[\alpha + 2(n + 1)]\}$$
$$= y_{1/2} \exp\{s'^2/2\} \quad (15)$$

In connection with y_m, there are some other formulas which may be useful, at least as a warning against using eq. (1), when it is intended for ideally homogeneous fractions, to calculate, for whole samples, average DP such as x_n, x_w, x_s, from the measured values of y_m: it is quite obvious that this procedure is not correct, particularly for broad distributions, but nevertheless this fact is often neglected. Such formulas are

$$y_m = K \exp\{(\gamma^2/4)(\alpha + 1)\} x_n{}^\alpha \quad (16)$$

$$y_m = K \exp\{(\gamma^2/4)(\alpha - 1)\} x_w{}^\alpha \quad (17)$$

$$y_m = K \exp\{(\gamma^2/4)(\alpha - 3)4 x_z{}^\alpha \quad (18)$$

It is evident that the DWD formula suggested by Lansing and Kraemer[29] is a particular case of eq. (2) when $n = 0$. The physical meaning of the Lansing-Kraemer formula is that the distribution *by number* of the macromolecules can be expressed by the normal error formula as a function of a variable which is itself a linear function of the logarithm of the DP.

In a similar manner, the distribution formula suggested by Wesslau[1] is a particular case of eq. (2) when $n = -1$. The physical meaning of Wesslau's formula is that the distribution *by weight* of the macromolecules can be expressed as defined above.

But it has been seen now that Feature A alone does not allow a choice of the exponent n, hence a choice between the two formulas.

More generally it can be said that, if a DWD formula such as eq. (2) is valid, by introducing an auxiliary variable t defined by eq. (5), the DWD function is transformed into a function, eq. (6), of the Gauss type, and in a quite similar manner a new auxiliary variable:

$$t' = [(2)^{1/2}/\gamma](\ln(x/x_0) - (n/2)\gamma^2) \quad (5')$$

can be defined (also a linear function of $\ln x$) so that the differential function of the distribution *by number:*

$$\bar{n}(x)dx = (1/x)w(x)dw$$

is transformed into a function of the Gauss type. It is immediately seen that, by combining eqs. (2) and (5'), under the normalization condition:

$$\int_0^\infty \bar{n}(x)dx = \int_{-\infty}^\infty \bar{n}(t')dt' = 1/x_n \quad (3')$$

which is equivalent to eq. (3), there follows:

$$\bar{n}(t')dt' = (1/x_n)[1/(2\pi)^{1/2}]\exp\{-t'^2/2\} dt' \quad (6')$$

Thus, when Feature A is verified, the differential distribution *by weight as well as by number* can be expressed by a Gauss formula as functions of some particular auxiliary variables which are, in their turn, linear functions of the log x.

In the next section a possible physical meaning of such auxiliary variables will be suggested.

Feature B

From the experimental data, particularly of ref. 1, it appears that, for the majority of the examined LPP samples, the distribution parameters γ and x_0 *tend* to be related with each other by

$$x_{1/2} = p \exp\{q\gamma\} \quad (19)$$

where p and q are nearly constant coefficients for all samples.

Attention has been already drawn[5] to the fact that the coefficient p (a degree of polymerization) is of the order of magnitude of the unity, or more exactly that it is close to the value *two*. In subsequent work it will be shown that the experimental data satisfy eq. (19) rather well, particularly for samples which better satisfy the straight-line condition termed Feature A. By assuming

$$p = 2 \quad (20)$$

it is found for nearly all samples that

$$q = 2.75 \pm 0.25 \quad (21)$$

Feature C

Let us now consider eq. (15). It states a necessary condition which must be satisfied by the quantity y_m and by the distribution parameters s' and $y_{1/2}$. The actual experimental data (see particularly ref. 1 where y is the intrinsic viscosity) show that this condition, eq. (15), is poorly satisfied: the values of y_m calculated by means of eq. (15) are larger than those measured; the larger y_m, the greater is this discrepancy.

This fact is physically equivalent to the statement made by Tung[4] that the Wesslau formula, hence also eq. (2), tends to exaggerate the high MW end of the distribution.

Feature D

Wesslau[8] has reached the noteworthy result of obtaining narrower MW distributions of LPP samples by means of chemical variations of the catalytic system. The new distributions obtained in this way also show stronger divergences from the straight line plots, as defined by Feature A.

According to Wesslau,[8] this result is in contradiction with the "working hypothesis 1" assumed by him, that "the shape of the MW distribution is determined *only* from the heterogeneous character of the polymerization reaction" and that "the *heterogeneity* of the catalyst is a *necessary and sufficient* condition to obtain a polymer having a *broad MW* distribution" (our *italics*). This author identifies this hypothesis 1 with the statement[5] that the MW distribution of LPP shows an analytical picture quite different from the one of, e.g., free radical polymers, and: "that this difference must be explained as a consequence of the different kind of action of the new catalysts..."

It is pointed out, now, that this statement, on which the present analysis is based, is quite different from hypothesis 1 of Wesslau; furthermore, in the writer's opinion, such hypothesis cannot *a priori* be accepted because: (*a*) It is not permissible to take into account *only one* of the catalytic circumstances, assuming it as a "necessary and sufficient condition" for determining the shape of the MW distribution. In fact, this latter results from the contribution of many agents and conditions. It is, of course, "necessary" to take an outstanding catalytic feature into account; however, this cannot be assumed "sufficient" as well. (*b*) It has been pointed out already that the most important feature is not that the MW distribution is broad or narrow, but the analytical type of the distribution itself.

As far as the "heterogeneity" of the catalyst is concerned, in Sections III and V of this work some considerations will be made on this topic and on its possible influence on the MW distribution.

For now, the following is stressed: Features C and D show that an interpretation of the MW distribution which will allow the possibility of deviations from the type of distribution characterized by Features A and B is to be sought after. Such a distribution type, which was observed in the majority of the hitherto investigated samples, could then be considered as a sort of "normal" or "most probable" MW distribution in the case of these new catalytic systems.

III. GENERAL SCHEME OF THE POLYMERIZATION KINETICS

Here are listed the features of the polymerization mechanism,[9-19] which are the most significant from the point of view of the present investigation:

(*1*) The catalytic suspensions (or solutions) are characterized by the presence of "*active centers*" (AC) having a long lasting and fairly constant (or slowly decaying) activity, even in the absence of monomer.

Although in the case of the LPP samples considered[1-8] as well as in the stereospecific polymerizations,[9-19] the heterogeneity of at least one of the catalytic components can be taken for granted, the writer's opinion is that, at this point of the present analysis, it is an unnecessary limitation to suppose that the AC must be only heterogeneous.

(*2*) The molecular growth occurring through the action of such AC can be interrupted by various growth breaking agents; at least four different types of such agents have been distinguished.[16] The majority of them also behaves as reactivation agents, i.e., when a dead molecule is detached from its parent AC, the latter can again start the growth of a new macromolecule when fresh monomer comes in contact with it.

(3) The average lifetime (or the average individual time of growth) of any single macromolecule appears to be very short, and the rate of growth of the chains seems to be very large (as compared with the rates of the other processes involved). According to Natta,[17] the molecular growth may be interpreted as a catalyzed stepwise addition, which can therefore take up high rates, at the limit, as a chain reaction.

(*4*) It appears[19] that a higher propagation rate is associated to the AC producing the longer polymer chains. In Ref. 19 such differences in rate are also associated to different stereospecificity. But in the case of polyethylene this last feature appears to be irrelevant; moreover, in the present analysis this result[19] will be purposely interpreted in the more general meaning expressed above. Thus, it may be considered at least as a working hypothesis, suggested from some experimental facts and until now, not contradicted by any of them.

IV. INTERPRETATION OF THE FEATURES OF MW DISTRIBUTION

Widely varying and often very broad MW distributions have been found for free radical poly-

merizations in high pressure polyethylenes.[26,28,30−32] They have been explained as a consequence of chain transfer to dead polymer giving rise to long branching.[28,33−36]

But it is unlikely that chain transfer to polymer and the long branching connected with it play any relevant part in the building up of the polymers considered here, particularly of LPP, because: (1) there is experimental evidence[4,33,33] that LPP has a mainly linear and not branched structure; and (2) chain transfer to polymer must be ruled out if the mechanism suggested by Natta, summarized in the former section, is accepted, as is done here.

On the basis of such considerations it is assumed that:

(1) The macromolecules considered here are linear; hence[27] they (as well as their distribution) can be characterized by a single variable, the DP or any quantity which is connected to the DP by a one-to-one relationship.

(2) It is possible to state such a one-to-one relationship between the DP and the "lifetimes" (or the times of growth) of the single macromolecules. Any macromolecule can thus be characterized by its DP as well as by its lifetime (LT); the MW distribution too can be expressed as a function of the lifetimes.

The interpretation of the MW distribution which will be given now is based on the consideration of the LT distribution and on a relationship between LT and DP. A more detailed analysis of the LT distribution on the basis of kinetic data will be sought in subsequent work. At this point a first-order approximation will be suggested, based on the following two hypotheses, which appear to be in agreement with the general kinetic scheme summarized in the former section.

Hypothesis I

Owing to the manifold growth-breaking and reactivating agents, the LT are distributed as a population (in the statistical meaning) of accidental events *tending* to distribute themselves at random about a mean.

It is generally accepted that the *most probable* distribution of such events is expressed by the Gauss function (or normal error function). Hence, by indicating with the symbol z the LT, the number $d\bar{n}$ of macromolecules having LT lasting from z to $z + dz$ is expressed by

$$d\bar{n} = [N/vz_0 (2\pi)^{1/2}] \exp \left\{ -\frac{1}{2}[(z - z_0)/(vz_0)]^2 \right\} dz \quad (22)$$

where N is the total number of macromolecules in the sample, z_0 is the mean (or the most probable) value of the LT, and v is a number such that the product vz_0 represents the "standard deviation" of the z from their mean value z_0.

It should be pointed out that in eq. (22) a normalization condition is implicit which differs from the one expressed by eqs. (3) and (3'); namely, it is stated

$$\Sigma \, d\bar{n} = N \quad \text{or} \quad \Sigma \, (d\bar{n}/N) = 1 \quad (3'')$$

Under such condition, eq. (6') becomes

$$\bar{n}(t') \, dt' = \frac{1}{(2\pi)^{1/2}} \exp \left\{ -\frac{t'^2}{2} \right\} dt' \quad (6'')$$

and the normalization factor A of eq. (2) will have the value:

$$A = [1/\gamma(\pi)^{1/2}] \, [1/(x_p')^n] \quad (4')$$

instead of the value given by eq. (4), which can also be written:

$$A = [1/\gamma(\pi)^{1/2}] \, [1/(x_m')^{n+1}] \quad (4'')$$

Hypothesis II

By taking into account item (3) of Section III, it is supposed that the macromolecular growth can be considered as a chain reaction, in the physical meaning of the term; that is, it is assumed that if the quantity x (the DP) is the result of such a reaction, the rate of growth of x is no longer constant, but it is an increasing function of the instantaneous value of x; in first approximation, the rate is assumed proportional to the function, namely

$$dx = hx\,dz \quad (23)$$

where h (a reciprocal time) is the rate of the relative growth. The integral of eq. (23) is

$$x = a \exp \{hz\} \quad (24)$$

where a is the *initial degree of polymerization*.

From the results obtained by Natta and co-workers,[18,19] it appears that the activator radical is found to be incorporated within the macromolecular chain, and that the most frequent growth breaking and reactivating agents are those resulting from chain transfer to monomer or from the action of the organometallic activator (whose radicals have dimensions of the same order of magnitude of the monomer units[14−17]). Hence, a value close to *two* can be expected for a, namely close to the value found by experiment of the coefficient p in eq. (19).

By accepting Hypothesis I, hence eq. (22), the latter can be compared with eq. (6″). It is immediately seen that they become equal if it is assumed that

$$\frac{z - z_0}{v z_0} = t' = \frac{(2)^{1/2}}{\gamma}\left(\ln\frac{x}{x_0} - \frac{n}{2}\gamma^2\right) \quad (25)$$

So, by combining eqs. (22) and (25), it follows:

$$\bar{n}(x)\,dx = \frac{w(x)dx}{dx}$$

$$= A'x^{n-1}\exp\left\{-\left(\frac{1}{\gamma}\ln\frac{x}{x_0}\right)^2\right\}dx \quad (2')$$

where A' is defined by eq. (4′); eq. (2′) is equivalent to eq. (2), when it is taken into account that the normalization condition of eq. (2) is eq. (3) and the one of eq. (2′) eq. (3′).

It is to be pointed out that eq. (25) attributes to the auxiliary variable t' the physical meaning of being a particular measure of the LT, namely, their relative deviation from their mean value z_0.

Now also Hypothesis II is taken into account; it is immediately seen that eq. (25) satisfies the differential equation (23), which is the analytical expression of this hypothesis, when it is stated:

$$\gamma = (2)^{1/2}hvz_0 \quad (26)$$

Hence Hypothesis II is already implicit in eq. (25). By comparing eqs. (25) and (24), we get:

$$a = x_0\exp\left\{(n\gamma^2/2) - hz_0\right\} \quad (27)$$

When eqs. (8) and (10′) are taken into account, from eq. (27) the eq. (26) and the two following equivalent relationships are obtained:

$$x_p' = a\exp\left\{hz_0\right\} \quad (28)$$

$$x_{1/2} = a\exp\left\{\frac{\gamma^2}{2} + \frac{1}{v}\frac{\gamma}{(2)^{1/2}}\right\} = a\exp\left\{s^2 + \frac{s}{v}\right\}$$

$$(29)$$

Equation (28) means that when $z = z_0$, the DP takes up its most probable value; this result is consistent with the present interpretation.

Hence, from Hypotheses I and II, a MW distribution showing Feature A is obtained. But eq. (29) states a relationship between $x_{1/2}$ and γ which can be confronted with eq. (19), the expression of Feature B.

It has already been observed that, by taking $a = p$, the experimental value of p is justified; but the exponent in eq. (29) is substantially different from the one of eq. (19), the latter being a

linear expression of γ while the former is a second-order expression of γ.

Hence Feature B is *not* in agreement with Hypotheses I and II. A physical meaning of this discrepancy will now be sought.

Although doing this is not in agreement with Hypothesis I (where the distribution *by number* is concerned), the variable t will be put in eq. (25) instead of the t': i.e.,

$$\frac{(z - z_0)}{v z_0} = t = \left[\frac{(2)^{1/2}}{\gamma}\right]\left(\ln\frac{x}{x_0} - \frac{n+1}{2}\gamma^2\right) (25')$$

In the same manner as for t', eq. (26) is obtained, together with

$$x_p' = a\exp\left\{-(\gamma^2/2) + hz_0\right\} \quad (30)$$

and

$$x_{1/2} = a\exp\left\{\gamma/(2)^{1/2}v\right\} = a\exp\left\{s/v\right\} \quad (31)$$

Equation (31) is equivalent to eq. (19), when it is defined:

$$q = 1/(2)^{1/2}v \quad (32)$$

But eq. (30) is no longer consistent with the significance of "most probable DP" which is stated by this interpretation, and which was no longer to be expected, since Hypothesis I has been modified.

It will now be seen that Feature B is in agreement with a new assumption which can be termed; "modified Hypothesis I," whose physical meaning will be stated now.

In the next section some further criticism will be given of the hypotheses introduced here; but for now it is possible to presume that the actual distribution of the LT instead of being expressed by the simple Gauss formula, is "perturbed" by factors limiting the chain growth; let us suppose that the longer chains have a higher probability of being detached from the parent AC than the shorter ones. This can bring about negative skewness in the LT distribution, as well as a displacement of the maximum x_p' toward the lowest DP.

Let us suppose, further, that such "perturbation" of the simple Gauss distribution can be represented, in a first approximation, by a factor proportional to the reciprocal DP; instead of eq. (22) it can be stated:

$$d\bar{n} = \frac{C}{x}\exp\left\{-\tfrac{1}{2}\left(\frac{z - z_0}{v z_0}\right)^2\right\}dz \quad (33)$$

where C is a normalization factor. It is immediately seen that eq. (33) is the analytical expression

of the modified Hypothesis I; indeed, it can be written:

$$x\,d\bar{n} = dw = C \exp\left\{-\frac{1}{2}\left(\frac{z-z_0}{vz_0}\right)^2\right\} dz \quad (33')$$

The left-hand side of this equation is the differential of the distribution *by weight*. Hence, when the modified Hypothesis I, namely eq. (33), is accepted, eq. (25') must be stated instead of eq. (25). As is shown by eq. (31), Feature B is just a consequence of eq. (25').

Equation (30) must be now justified. By substituting eq. (26) in eq. (31): $x_{1/2} = x_0$ and $x_p' = x_0 \exp\left\{-(\gamma^2/2)\right\}$.

If eqs. (8) and (10') are taken into account, both these last relationships are possible only if $n = -1$.

It is seen, thus, that the consideration of Feature B, together with the present interpretation, allows an evaluation of the exponential parameter n, which was not possible on the basis of Feature A alone.

Furthermore, a physical meaning of n is now suggested: n should be a measure of a particular "perturbation" in the LT distribution, with respect to the simple Gauss distribution. This latter is characterized by $n = 0$, and the value $x_0 = a \exp\left\{hz_0\right\}$, as stated by eq. (10'), is the most probable DP only for the unperturbed LT distribution; but x_0 no longer coincides with x_p' when $n \neq 0$ (or for perturbed LT distributions). Feature B indicates a negative value of n, close to -1.

It is interesting to note the following:

(*a*) A negative exponent n has a physical significance analogous to that of a negative skewness in the LT distribution; and, inversely, positive n corresponds to positive skewness. Perturbations of the Gauss distribution which can be represented by x^n bring about a displacement of the maximum in the differential LT distribution, rather than a true skewness of it. In subsequent work the polydispersion of free radical polymers will be dealt with by means of the study of the LT distribution of growing chains. It will be seen that in free radical polymerization the most frequent instance is that of positive skewness or positive n values, while in the catalytic systems considered here it appears that the negative n values are the rule.

(*b*) The present interpretation and the consequent evaluation of the n exponent state that the first distribution formula proposed by Wesslau,[1] with $n = -1$, is the most valid, giving to the parameter x_0 its true physical meaning, as specified

here, although in ref. 1 the choice of $n = -1$ was not justified.

Some considerations will be made about the parameter q of eq. (19); eq. (32), together with the experimental results summarized by eq. (21), states that the unperturbed "most probable distribution" defined here is characterized by standard deviations which are all about $1/4$ of the mean value of the LTs.

As far as the field of variability of the LTs are concerned, in the integrations carried out for normalization it is assumed that t and t' vary between $-\infty$ and $+\infty$, corresponding to x varying between 0 and $+\infty$. But the limits for z are obviously 0 and $+\infty$; hence eqs. (25) and (25') can be accepted only if the value: $\exp\left\{-1/_2v^2\right\}$ is practically equal to zero. By supposing that the limit of accuracy in the experimental determination of the weight per cents in the CWD curve is 1% (which in practice is a rather stringent limit), it follows that

$$[1/(2\pi)^{1/2}] \int_{-\infty}^{(-1/v)} \exp\left\{-1/_2t^2\right\} dt < 0.01$$

which happens when: $1/v > 2.33$ or $q > 1.55$.

It is seen from eq. (21) that for those LPP samples which show Features A and B sufficiently to allow the determination of the parameter q, this last condition is largely satisfied, hence the accuracy in the present formulation is greater than that requested by the actual experimental accuracy.

Lastly, it is to be noted that the formulas stated in this section allow the determination of the product hz_0 (a number), but an independent determination of the factors h and z_0 is not possible; it is expected, indeed, that these typically dynamic parameters can be determined only by means of investigations on the polymerization kinetics, and that the study of the distribution alone (depending on the ratio of the kinetic parameters) is not sufficient for this purpose. On the contrary, it is seen from eqs. (26) and (32) that the statistical parameter v is directly related to the distribution features.

IV. CRITICISM OF HYPOTHESES I AND II

It has been already suggested that Hypotheses I and II and the corresponding eqs. (22) and (23) are simplifications (probably, oversimplifications) of the actual phenomena occurring in these polymerization processes; they must be considered more properly as limit-hypotheses (*Grenzhypothesen*).

In the former section it was seen that Hypothesis I had to be modified to fit in with Feature B, namely it has been necessary to introduce a particular correction or "perturbation" of the simple Gauss distribution of the LTs. Similarly, other kinds of perturbations can be expected, different from the ones depicted by a factor x^n. This can explain the experimental facts summarized as Feature D; in particular, the results of Wesslau[8] indicate perturbations of the leptokurtic type. Only a more detailed analysis of the LT distribution and of its dependence on the polymerization kinetics may allow to state a surer connection between the polymerization conditions and the distribution features.

Hypothesis II, at the present state of investigations, appears the one less firmly supported by experimental evidence, the strongest evidence consisting, perhaps, in the fact that it allows a consistent analytical interpretation of the observed distribution features.

It may be that the idea of a catalyzed stepwise addition proceeding as a chain reaction can be accepted more easily remembering the advice given by Semenov,[39] that one must not deal "exclusively with the elementary chemical act" but that one has to consider the whole "system of elementary acts, i.e., all problems connected with actually occurring chemical changes." In the present instance, it may happen that, while the mechanism of any single elementary addition act remains unchanged, the probability of its occurrence can be modified (in the given case, increased) by the presence of the already formed but still growing macromolecular chain.

Such an "autocatalysis" can be produced, e.g., as follows:

(a) Any single exothermic addition reaction may bring about a local overheating in the surroundings of an AC. Something of that sort has been observed by Natta and Mantica[40] in the case of the anionic stepwise addition of ethylene oxide to alcohols, where the reaction rate of each successive step is higher, owing to an activation attributable to the preceding highly exothermic step.

(b) As was suggested to the writer by Luzzati,[41] the already formed and growing polymer molecule may increase the solubility of the monomer in the surroundings of the parent AC; in this way, the local monomer concentration, hence the probability of occurrence of the single addition reactions is increased.

It is evident that the greater is the rate of chain propagation (which was actually found to be high[18,19]), the more important are both these effects. Furthermore, they must be stronger also when the ACs have a more stationary position; this may happen when the ACs are heterogeneous, that is when they are bonded to a solid surface or to a particle having at least a Brownian size. Hence, it appears that the heterogeneity of the catalysts is more clearly related with Hypothesis II, concerning the law connecting the DPs with the LTs; but it is to be expected that the heterogeneity of the catalysts plays a relevant part also in the determination of the statistics of the LT distribution, considered by Hypothesis I.

Further, it is to be expected that both these effects of "autocatalysis" of the growing chain diminish when the chain grows beyond certain limits, that is, that these effects undergo saturation. It follows that the rate of the macromolecular growth, beyond a certain chain length, must be less than the one resulting from eq. (23). This fact is confirmed by what has been summarized as Feature C. As was already observed by Wesslau,[1] an overestimation of the high MW end of the distribution (where eq. (1) itself, perhaps, can no longer be used) is more noticed in the determination of the average intrinsic viscosity of the whole sample than in the overall shape of the MW distribution curve (Feature A).

Finally, it is observed that the distribution formula suggested by Lansing and Kraemer has been found of little use to represent the MW distribution of synthetic polymers obtained by the free radical or by the polycondensation mechanism. The theories of such polymerizations, developed particularly by Flory,[42] led to analytically different formulas, which proved to be in better agreement with the experimental data.

Lansing and Kraemer have found that their formula is suitable for describing the MW distributions of natural gelatins (as was obtained from the experiments of Krishnamurti and Svedberg[43]) and of other natural polymers; similar results, concerning also natural polymers, have been recently obtained by Ciferri and Daune.[44]

Although the polydispersity of the investigated natural polymers is in general rather narrow, hence a MW distribution formula can be stated in a less reliable way, this fact may bring some further support to the idea of a qualitative analogy existing between the catalytic methods considered here and the polymerizations occurring in some biologic processes. A quantitative difference is apparent, which is expressed by higher values of the distribu-

tion parameter γ in the synthetic new polymers than in natural polymers. From eq. (26) it appears that, for equal values of the product hz_0 (namely, for equal average extent of polymerization), larger values of γ mean larger v or larger standard deviations, hence greater randomness in the synthetic processes than in the biological ones.

Thus, from the present interpretation of the distribution features of polymers obtained from the new catalytic processes considered here it appears that it is possible, as already suggested by Natta,[45] that a deeper knowledge of such processes can bring new light on some polymerizations (which, too, are often stereospecific) occurring in living matter.

References

1. H. Wesslau, *Makromol. Chem.*, **20.** 111 (1956).
2. R. S. Aries and A. P. Sachs, *J. Polymer Sci.*, **21**, 551 (1956).
3. P. S. Francis, R. C. Cooke, J. H. Elliott, paper presented at the American Chemical Society Meeting, Atlantic City, September, 1956.
4. L. H. Tung, *J. Polymer Sci.*, **24**, 333 (1957).
5. C. Mussa I. V., *J. Polymer Sci.*, **26** 67 (1957).
6. C. Mussa I. V., *J. Polymer Sci.*, **29**, 171 (1958).
7. H. Wesslau, *Makromol. Chem.*, **26**, 96 (1958).
8. H. Wesslau, *Makromol. Chem.*, **26.** 102 (1958).
9. G. Natta, *Chim. e ind. (Milan)*, **37**, 888 (1955).
10. G. Natta, *Makromol. Chem.*, **16**, 213 (1955).
11. G. Natta, *Chim. e ind. (Milan)*, **38**, 124 (1956).
12. G. Natta, I. Pasquon, and E. Giachetti, *Makromol. Chem.*, **24**, 258 (1957).
13. C. Natta, I. Pasquon, and E. Giachetti, *Angew. Chem.*, **69**, 213 (1957).
14. G. Natta, I. Pasquon, and E. Giachetti, *Chim. e ind. (Milan)*, **39**, 933 (1957).
15. G. Natta, I. Pasquon, and E. Giachetti, *Chim. e ind. (Milan)*, **39**, 1002 (1957).
16. G. Natta, I. Pasquon, and E. Giachetti, *Chim. e ind. (Milan)*, **40**, 97 (1958).
17. G. Natta, I. Pasquon, E. Giachetti, and F. Scalari *Chim. e ind. (Milan)*, **40**, 103 (1958).
18. G. Natta, I. Pasquon, E. Giachetti, and G. Pajaro, *Chim. e. ind (Milan)*, **40**, 267 (1958).
19. G. Natta, *J. Polymer Sci.*, **34**, 21 (1959).
20. K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Chim. e ind. (Milan)*, **37**, 881 (1955); *Angew. Chem.*, **67**, 426 (1955).
21. A. Gilchrist, *J. Polymer Sci.*, **34**, 49 (1959).
22. A. Orzechowski, *J. Polymer Sci.*, **34**, 65 (1959).
23. L. Trossarelli, E. Campi, and G. Saini, *J. Polymer Sci.*, in press.
24. L. Freund and M. Daune, *J. Polymer Sci.*, **29**, 161 (1958).
25. R. F. Boyer, *Ind. Eng., Anal. Ed.*, **18**, 342 (1946).
26. L. H. Tung, *J. Polymer Sci.*, **20**, 495 (1956).
27. C. Mussa I. V., *J. Polymer Sci.*, **25.** 448 (1957).
28. C. Mussa I. V., *J. Polymer Sci.*, **28.** 587 (1958).
29. W. D. Lansing and E. O. Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935).

30. F. W. Billmeyer, Jr., *J. Am. Chem. Soc.*, **75**, 6118 (1953).
31. L. Nicolas, *Makromol. Chem.*, **24**, 173 (1957).
32. A. Nasini and C. Mussa, *Makromol. Chem.*, **22**, 59 (1957).
33. M. J. Roedel, *J. Am. Chem. Soc.*, **75**, 6110 (1953).
34. C. H. Bamford and H. Tompa, *J. Polymer Sci.*, **10**, 345 (1953).
35. J. K. Beasley, *J. Am. Chem. Soc.*, **75**, 6123 (1953).
36. C. H. Bamford and H. Tompa, *Trans. Faraday Soc.*, **50**, 1097 (1954).
37. K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.*, **67**, 541 (1951).
38. Q. A. Trementozzi, *J. Polymer Sci.*, **22**, 187 (1956).
39. N. Semenov, *Chemical Kinetics and Chain Reactions*, Oxford Univ. Press, 1935.
40. G. Natta and E. Mantica, *J. Am. Chem. Soc.*, **74**, 3152 (1952).
41. V. Luzzati, Centre National de Recherches sur les Macromolecules, Strasbourg. Private communication.
42. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953.
43. K. Krishnamurti, and T. Svedberg, *J. Am. Chem. Soc.*, **52**, 2897 (1930).
44. A. Ciferri and M. Daune, *J. Polymer Sci.*, **27**, 581 (1958); *Ricerca sci.*, **28**, 508 (1958).
45. G. Natta, *Angew. Chem.*, **68**, 393 (1956).

Synopsis

Some features of the molecular weight distributions found by experiment for low pressure polyethylenes are examined; an analytical interpretation of them is suggested which is in agreement with the polymerization mechanism resulting from kinetic investigations of Natta and co-workers. Such interpretation is based on the consideration of the distribution of the individual times of growth (or of the "lifetimes") of the single macromolecules. It is assumed that (a) these lifetimes tend to be distributed according to the Gauss formula, such as a series of events tending to be distributed at random about a mean; and (b) the growth of any single macromolecule proceeds at a rate which can be considered as the rate of a chain reaction. Possible deviations from such simplified scheme are taken into account. A distribution formula of a generalized Lansing-Kraemer type is deduced, giving an explanation of all the observed features of the molecular weight distribution.

Résumé

On examine quelques particularités des distributions des poids moléculaires observées dans des polyéthylenes de basse pression. On en donne une interprétation analytique qui est en accord avec le mécanisme de formation résultant des études cinétiques de Natta et collaborateurs. Cette interprétation est fondée sur la considération de la distribution des durées de propagation individuelles (ou "durées de vie") de chaque macromolécule. On suppose que: (a) ces durées de vie tendent à être distribuées selon une formule de Gauss, comme des événements qui tendent a se distribuer au hasard autour d'une moyenne: (b) la croissance de chaque macromolécule marche à une allure qui peut être assimilée à celle d'une réaction en chaîne. Des déviations possibles de ce schéma simplifié ont été envisagées et introduites dans le calcul. On déduit une formule de distribution

du type de Lansing-Kraemer généralisée, qui fournit une explication de toutes les caractéristiques de distribution des poids mléoculaires.

Zusammenfassung

In der vorliegenden Arbeit werden einige Eigentümlichkeiten der experimentell erhaltenen Molekulargewichtsverteilung von Niederdruckpolyäthylen näher untersucht und eine analytische Deutung derselben, die mit dem Bildungsmechanismus entsprechend den kinetischen Untersuchungen von Natta u. Mitarb. in Übereinstimmung steht, wird vorgeschlagen. Dieser Deutung liesen gewisse Annahmen über die Verteilung der individuellen Wachstums-dauern (oder "Lebensdauern") der einzelnen Makromoleküle zu Grunde. Es wird angenommen, dass: (a) diese Lebensdauern einer Gauss'schen Verteilung zustreben, so wie eine Reihe von Ereignissen, die sich zufälligerweise um einen Mittelwert verteilen; (b) der Verlauf des Wachstums der einzelnen Makromoleküle mit dem einer Kettenreaktion verglichen werden kann. Mögliche Abweichungen von einem solchen vereinfachten Schema werden in Betracht gezogen. Eine Verteilungsfunktion vom Typus einer verallgemeinerten Lansing-Kraemer-Verteilung wird abgeleitet. Damit ist eine Deutung aller beobachteten Eigentümlichkeiten der MG-Verteilung möglich.