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The Molecular Structure of Polyethylene. IV. Kinetic Calculations of the Effect of Branching on Molecular Weight Distribution[1]

BY J. K. BEASLEY

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The number and distribution of long chain branches, together with detailed molecular weight distribution functions, are calculated from kinetic equations describing the process of radical transfer to polymer. The presence of branching causes the molecular weight distribution to be broadened with the appearance of a long high molecular "tail" on the distribution curve. The ratio of the weight average to the number average molecular weight may become much higher than the ratio for linear polymers. There is a very broad distribution in the number of branches per molecule with a large fraction of the polymer remaining unbranched. The distribution functions and their averages are calculated in terms of two parameters: a, which is the reciprocal of the number average degree of polymerization of all the long chains, and β, a branching parameter derived here.

I. Introduction

Although the possibility that branching in polymers may occur by free radical transfer to polymer has been mentioned in the literature, no calculations have appeared which give molecular weight distributions resulting from such branching. Previous calculations have dealt with the type of branching which arises from multifunctional monomer units. Flory[2] has published numerous papers dealing with molecular weight distributions resulting from such branching. His calculations have been extended by Stockmayer[3] and Walling.[4] All of these calculations were statistical in nature and were based on the assumption of completely random location of branch points. But Flory[5] has stated that if the branching mechanism involves previously formed polymer, then the theory of molecular weight distribution cannot employ the assumption of completely random branch points.

In this paper, the calculations are based directly on the mechanism of radical transfer to polymer and the results specifically include reaction rate constants. Although these calculations have been applied primarily to polyethylene, the results can be expected to apply to any addition polymer subject only to the restrictions imposed by the conditions and assumptions described here. These results show that the amount of long chain branching depends on the ratio of the rate constant for transfer to polymer compared to the rate constant for propagation. Unless this ratio is zero, and it is difficult to imagine that the transfer rate is absolutely zero, the polymer must contain some branching. However, this ratio may be so small for many polymers that it would be very difficult to detect branching experimentally.

II. Conditions and Assumptions

For the sake of mathematical simplicity, a special type of polymerization system is considered: one in which the concentrations of all molecular species remain constant with time in a one-phase system. This condition could be achieved in continuous polymerization by withdrawing the polymer-monomer mixture at the same rate at which monomer is fed to the system. The presence or absence of solvent should not affect the results of these calculations. Sufficient mixing would be required to maintain uniform concentrations of all molecular species throughout the system. Although these conditions cannot be obtained exactly in experimental polymerization, they can be approximated closely enough to provide comparisons between theoretical and experimental results.

The same reaction mechanisms would apply in non-steady state polymerizations. However, the differential equations used here would be slightly different; their solution would be much more difficult and would involve numerical computations instead of analytical solutions.

This paper deals with *long chain branching exclusively*. The short chains which are formed by transient six-membered rings are assumed to be distributed at random along all of the long chains; they cannot be part of the normal distribution of long chains calculated here because of their relatively high frequency of occurrence due to a different reaction mechanism. Long chain branches are formed primarily by intermolecular free radical transfer. However, the few chains which are formed by intramolecular transfer at a distance greater than about six carbon atoms back along the chain may be considered as part of the long chain distribution without introducing serious error.

The distribution of lengths of long chain branches assumed here is the familiar exponential type of distribution which applies when the chains are terminated either by transfer or by disproportionation with another radical.

It is assumed that the probability of free radical transfer to a given molecule with subsequent growth of another long chain branch is proportional to the number of monomer units in the molecule. This assumption cannot be exact for very large molecules where some shielding of the inner portions of the molecules must occur. However, this assumption is a logical one to make and it does enable an analytical solution of the equations to be obtained.

A conventional reaction mechanism is assumed: decomposition of an initiator to give free radicals, propagation by the addition of monomer units, termination of two free radicals by disproportionation, transfer to monomer, and transfer to polymer (long chain branching). Activity coefficients are

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[1] Presented at the 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March 16, 1953.

[2] P. J. Flory, THIS JOURNAL, **63**, 3083, 3091, 3096 (1941); *J. Phys. Chem.*, **46**, 132 (1942); *Chem. Revs.*, **39**, 137 (1946); THIS JOURNAL, **69**, 30, 2893 (1947).

[3] W. H. Stockmayer, *J. Chem. Phys.*, 11, 45 (1943); **12**, 125 (1944); *J. Polymer Sci.*, **9**, 69 (1952).

[4] C. Walling, THIS JOURNAL, **67**, 441 (1945).

[5] P. J. Flory, *ibid.*, **69**, 2893 (1947).

assumed to be unity in all cases; however, they could be included if so desired.

III. Rate Equations

The following equations may be written for the system described above. Let

V = vol. of the reaction

q = rate of removal of contents (vol. per unit time)

$N_{b,x}$ = no. of moles of polymer per unit vol. having x monomer units and b long chain branch points

K_f = total rate of formation of new polymer molecules per unit vol.; this rate includes new polymer molecules formed from radicals resulting from decomposition of initiator and also those resulting from chain transfer to monomer

k_p = rate constant for propagation (addition of monomer units)

k_b = rate constant for transfer to polymer (long chain branching)

$n(x)$ = distribution function for long chains; mole fraction of long chains having x monomer units
For the exponential type of distribution assumed above
$n(x)\,\mathrm{d}x = \exp(-ax)\mathrm{d}(ax) = a\exp(-ax)\,\mathrm{d}x$

$1/a$ = number average number of monomer units per long chain

(M) = concn. of monomer (moles per unit vol.)

(P) = concn. of all polymer molecules (moles of combined monomer units per unit vol.)

$(R\cdot)$ = concn. of free radicals

t = time

Molecules having zero branch points and containing x monomer units are formed as new molecules; they may disappear by branching at a rate proportional to x or by being removed from the system. For the steady state conditions assumed above

$$\frac{\mathrm{d}N_{0,x}}{\mathrm{d}t} = K_f n(x) - k_b(x)(R\cdot)N_{0,x} - (q/V)N_{0,x} = 0 \quad (1)$$

Molecules having b long chain branch points and x monomer units are formed by the growth of a long chain branch on a molecule of $(b - 1)$ branch points; the total number of monomer units in the old molecule and the new branch must add to give x. These molecules also disappear by branching and by being removed from the system.

$$\frac{\mathrm{d}N_{b,x}}{\mathrm{d}t} = \sum_{y=0}^{y=x} [k_b(R\cdot)yN_{(b-1),y}][n(x-y)] - k_b(R\cdot)xN_{b,x} - (q/V)N_{b,x} = 0 \quad (2)$$

The summation in 2 may be approximated by an integration upon substitution of the assumed form for $n(x)$. Solving for $N_{b,x}$

$$N_{b,x} = \frac{(V/q)\int_{y=0}^{y=x}[yN_{(b-1),y}]\,a\exp[-a(x-y)]\mathrm{d}y}{1 + k_b(R\cdot)(V/q)(1/a)(ax)} \quad (3)$$

From 1

$$N_{0,x}\,\mathrm{d}x = \frac{K_f(V/q)\exp(-ax)\,d(ax)}{1 + k_b(R\cdot)(V/q)(1/a)(ax)} \quad (4)$$

Equation 4 may be substituted in 3 to obtain a solution for $N_{1,x}$. By repeated substitution in 3, a solution for $N_{b,x}$ may be obtained for any value of b.

The grouping of parameters in the denominator of 3 or 4 may be conveniently replaced by a new parameter, β. By definition

$$\beta = k_b(R\cdot)(V/q)(1/a) \quad (5)$$

Considering all of the polymer, for the steady state conditions assumed above

$$\frac{\mathrm{d}(P)}{\mathrm{d}t} = k_p(R\cdot)(M) - (q/V)(P) = 0 \quad (6)$$

Then the concentration of free radicals must be

$$(R\cdot) = \frac{(q/V)(P)}{k_p(M)} \quad (7)$$

Substitution of 7 in 5 shows that

$$\beta = \frac{k_b(P)(1/a)}{k_p(M)} = \frac{k_b(R\cdot)(P)(1/a)}{k_p(R\cdot)(M)} \quad (8)$$

Since $(1/a)$ is the average number of monomer units per long chain, β is the ratio of the rate of branching times the average chain length compared to the rate of propagation (addition of monomer units). In other words, β is the ratio of the total number of monomer units in branches (number of branches times the average branch length) compared to the total number of monomer units in the polymer. Obviously then, β must be restricted to values less than one.

IV. Distribution Functions for Branched Polymer

By repeated substitution in 3 the following general solution is obtained

$$N_{b,x}\,\mathrm{d}x = \frac{K_f(V/q)[(ax) - (1/\beta)\ln(1 + \beta ax)]^b\exp(-ax)\,\mathrm{d}(ax)}{b!\,(1 + \beta ax)} \quad (9)$$

The total number of moles (per unit volume) having x monomer units (N_x) is obtained by summing 9 over all numbers of long chain branch points.

$$N_x\,\mathrm{d}x = \sum_{b=0}^{b=\infty} N_{b,x}\,\mathrm{d}x = \frac{(V/q)K_f\mathrm{d}(ax)}{[1 + \beta ax]^{(1 + 1/\beta)}} \quad (10)$$

The total number of moles of polymer (per unit volume) is obtained by integrating 10

$$\int_{x=0}^{x=\infty} N_x\,\mathrm{d}x = (V/q)K_f \quad (11)$$

which must be true from the definition of V, q and K_f.

The corresponding mole fractions may be obtained by dividing 9 and 10 by 11. These results are also the "normalized" number distribution functions.

The weight of polymer per unit volume (for molecules having b branch points and x monomer units) may be obtained by multiplying the corresponding number of moles by the molecular weight of the polymer, mx, where m is the weight of one monomer unit. The total weight of polymer per unit volume is obtained by summing over all possible number of branch points and number of monomer units. This total weight is

$$\int_{x=0}^{\infty}\sum_{b=0}^{\infty} mxN_{0,x}\,\mathrm{d}x = \int_{x=0}^{\infty} mxN_x\,\mathrm{d}x = \frac{(V/q)K_f(1/a)m}{(1-\beta)} \quad (12)$$

The fraction by weight of the polymer having b branch points and x monomer units, $W_b(x)$, is obtained by multiplying 9 by the molecular weight and dividing by 12

$$W_b(x)\,\mathrm{d}x = \frac{(1-\beta)(ax)[(ax) - (1/\beta)\ln(1 + \beta ax)]^b\exp(-ax)\mathrm{d}(ax)}{b!\,(1 + \beta ax)} \quad (13)$$

The fraction by weight of the polymer having x monomer units (including all degrees of branching), $w(x)$, is obtained similarly from 10 and 12

$$W(x)\,\mathrm{d}x = \frac{(1-\beta)(ax)\,d(ax)}{[1+\beta ax]^{(1+1/\beta)}} \qquad (14)$$

Equations 13 and 14 are also the "normalized" weight distribution functions.

Figure 1 shows a plot of 14 for various values of β. (Actually $(1/a)W(x)$ is plotted as the ordinate; the abscissa is ax.) This figure illustrates the features which are to be expected from long chain branching. The curve labeled $\beta = 0$ represents the distribution which would be obtained in the absence of long chain branching. The other curves represent various degrees of long chain branching which increases with β. They illustrate the broadening of the molecular weight distribution with increasing amounts of branching. The insert in Fig. 1 illustrates the long high molecular weight "tail" which results from long chain branching and which has such a profound effect on the weight average molecular weight.

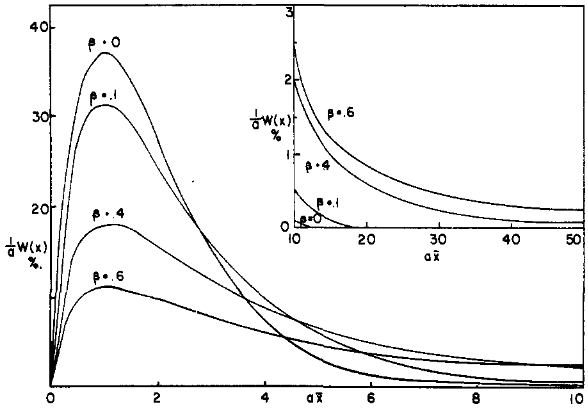

Fig. 1.—Calculated weight distribution functions for various degrees of branching.

V. Average Degree of Polymerization and Average Number of Branches

By definition the number average degree of polymerization, $\bar{X}_n$, is obtained by

$$\bar{X}_n = \frac{\int_{x=0}^{x=\infty} xN_x\,\mathrm{d}x}{\int_{x=0}^{x=\infty} N_x\,\mathrm{d}x} \qquad (15)$$

Substituting equation 10 and integrating

$$\bar{X}_n = \frac{1/a}{(1-\beta)} \text{ if } \beta < 1 \qquad (16)$$

Similarly, the weight average degree of polymerization, $\bar{X}_w$, is obtained from 14

$$\bar{X}_w = \frac{\int_{x=0}^{x=\infty} xW(x)\,\mathrm{d}x}{\int_{x=0}^{x=\infty} W(x)\,\mathrm{d}x} = \frac{(2/a)}{(1-2\beta)} \text{ if } \beta < 1/2 \qquad (17)$$

These two functions, $\bar{X}_n$ and $\bar{X}_w$, are plotted in Fig. 2. Both the number average and the weight average degree of polymerization increase with increasing β (when a is constant). However, the weight average increases rapidly as β approaches $^1/_2$ while the number average does not increase rapidly until β approaches one. Thus, the ratio of the weight average to the number average, which starts at 2 for unbranched polymer, increases to very large values as β approaches $^1/_2$.

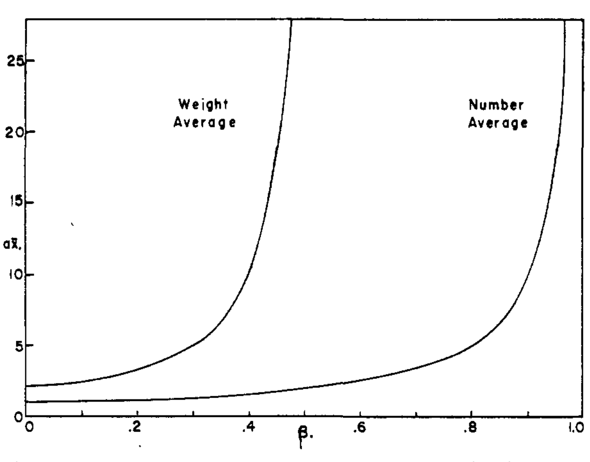

Fig. 2.—Calculated average degree of polymerization as a function of the branching parameter.

The weight average has no significance above $\beta = ^1/_2$ because the integral used in its calculation does not converge above $\beta = ^1/_2$. This difficulty does not arise for the distribution functions themselves nor for the number average until $\beta = 1$. Therefore, these terms do have significance between $\beta = ^1/_2$ and $\beta = 1$. Because of the definition of β, values of β greater than 1 are meaningless.

The average number of branch points per molecule may be obtained in an analogous manner. For all molecules having x monomer units, the average number of branch points is

$$(b)_x = \frac{\sum_{b=0}^{b=\infty} bN_{b,x}\,\mathrm{d}x}{\sum_{b=0}^{b=\infty} N_{b,x}\,\mathrm{d}x} = [ax - (1/\beta)\ln(1+\beta ax)] \qquad (18)$$

For the whole polymer, the number average number of branch points per molecule is

$$(b)_n = \frac{\int_{x=0}^{x=\infty} (b)_x N_x\,\mathrm{d}x}{\int_{x=0}^{x=\infty} N_x\,\mathrm{d}x} = \frac{1}{1-\beta} - 1 \qquad (19)$$

For the whole polymer, the weight average number of branch points per molecule is

$$(b)_w = \frac{\int_{x=0}^{x=\infty} (b)_x W(x)\,\mathrm{d}x}{\int_{x=0}^{x=\infty} W(x)\,\mathrm{d}x} = \frac{1}{(1-2\beta)(1-\beta)} - 1 \quad \text{when } \beta < 1/2 \qquad (20)$$

These two functions, 19 and 20, are shown in Fig. 3. The general shapes of the curves are similar to the curves for average degree of polymerization (Fig. 2), though of course the number of branch points is zero when $\beta = 0$ when there is no branching. Also, the weight average number of branch points has meaning only for $\beta < ^1/_2$.

For polymers having a finite weight average degree of polymerization, there can be only about one

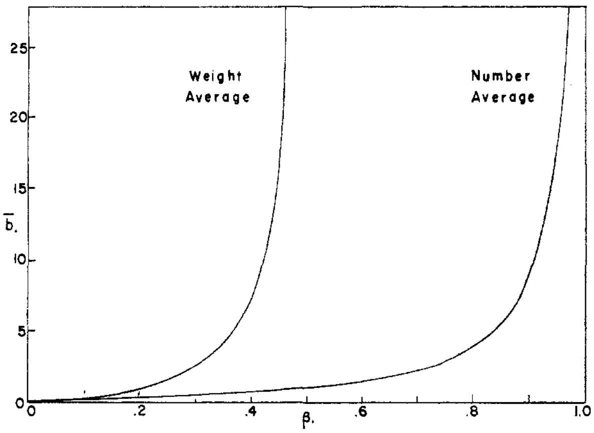

Fig. 3.—Calculated average number of branch points per molecule as a function of the branching parameter.

long chain branch point per molecule on a number average basis. Thus, the average number of branch points per molecule measured by Billmeyer,[6] and designated as n, must be greater than a number average and may approach a weight average.

This result also helps prove the existence of at least two branching mechanisms in polyethylene. The total number of chain ends as measured by infrared is much greater than three per molecule. Since only about one branch point (three chain ends) per molecule can arise from intermolecular free radical transfer, then another mechanism must be postulated to account for the much larger number of chain ends which are observed.

VI. Fraction of Unbranched Polymer

There is a very wide distribution in the number of branch points per molecule. See equation 18 for example. A significant fraction of the polymer has no long chain branch points. The mole fraction of unbranched molecules is

$$N_0 = \frac{\int_{x=0}^{x=\infty} N_{0,x}\, dx}{\int_{x=0}^{x=\infty} N_x\, dx} \qquad (21)$$

Using equations 9 and 10 and making the substitution $Z = (1/\beta)\ (1 + \beta a x)$

$$N_0 = (1/\beta) \exp(1/\beta) \int_{z=1/\beta}^{z=\infty} (1/Z) \exp(-Z)\, dZ \qquad (22)$$

This integral is the logarithmic integral. (For numerical values see *Tables of Functions*, Jahnke and Emde.)

The weight fraction of unbranched polymer is

$$W_0 = \int_{x=0}^{x=\infty} W_0(x)\, dx \qquad (23)$$

Substituting 13 and integrating

$$W_0 = (1/\beta)(1 - \beta)(1 - N_0) \qquad (24)$$

For example, when $\beta = 0.4$, $N_0 = 0.7586$, $W_0 = 0.3621$, and when $\beta = 0.5$, $N_0 = 0.7226$, $W_0 = 0.2774$.

VII. Comparison with Experimental Data

Few experimental data are available for a direct comparison with the theoretical relationships presented here. The results reported by Billmeyer[6] cannot be used because those polyethylenes were not prepared under the conditions assumed here for the sake of mathematical simplicity. However, there is complete qualitative agreement between Billmeyer's results and these theoretical results: (1) a broadened molecular weight distribution curve, (2) a relatively high ratio between weight average molecular weight and number average molecular weight, and (3) within fractions of a given polymer, an increase in the average number of branch points per molecule with increasing molecular weight (see equation 18).

A more direct comparison between theory and experiments could be obtained in the following manner: equation 16 can be solved for a and substituted in equation 8 to give

$$\beta = \frac{(k_b/k_p)[(P)/(M)](\bar{X}_n)}{1 + (k_b/k_p)[(P)/(M)](\bar{X}_n)} \qquad (25)$$

The ratio of the weight average degree of polymerization to the number average degree of polymerization should be a function of β alone. This result is obtained by dividing equation 17 by 16.

$$\bar{X}_w/\bar{X}_n = 2(1 - \beta)/(1 - 2\beta) \qquad (26)$$

Substituting 25 in 26

$$\frac{\bar{X}_w}{\bar{X}_n} = \frac{2}{1 - \frac{k_b}{k_p}(\bar{X}_n)\frac{(P)}{(M)}} \qquad (27)$$

Thus, when the polymerization conditions are such that k_b, k_p, and $\bar{X}_n$ do not change, then the ratio of the weight average to the number average degree of polymerization should be a function of polymer/monomer ratio, $(P)/(M)$, alone.

Figure 4 shows experimental results obtained on a series of polyethylenes prepared under conditions approximating the above requirements at different polymer/monomer ratios. The weight average and the number average degrees of polymerization were determined by Billmeyer.

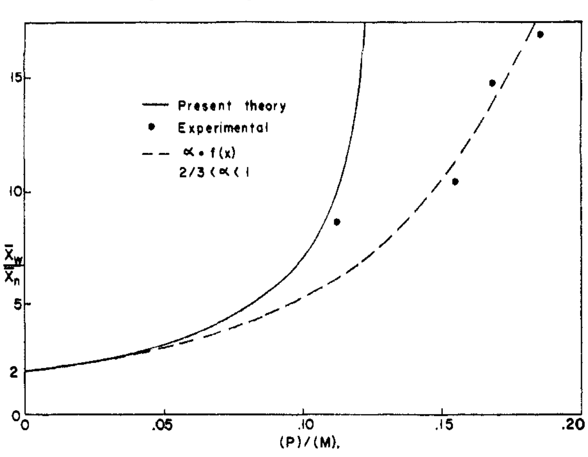

Fig. 4.—Ratio of weight average to number average degree of polymerization as a function of polymer/monomer ratio during polymerization.

The solid line on Fig. 4 represents the functional relationship derived here (equation 27) calculated for a value of 7.25 for $(k_b/k_p)(\bar{X}_n)$. By choosing other values the line could be made to pass through

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[6] F. W. Billmeyer, Jr., This Journal, **75**, 6118 (1953).

any one of the experimental points but not through all of them. It is evident that the ratio of molecular weights does increase with polymer/monomer ratio as predicted by this theory but the rate of increase is not so rapid as that predicted.

Experimental error might account for some of the deviations shown in Fig. 4, but there is also a good reason for expecting a lack of precision in the theory. The derivations were based on the assumption that the probability of free radical transfer to a given molecule with subsequent growth of another long chain branch is proportional to the number of monomer units in the molecule. This assumption might be expected to hold for small polymer molecules which would be well extended in solution and equally susceptible to free radical transfer at all points.

However, large, highly branched molecules could be expected to show some shielding effect so that the probability of branching must be somewhat less than proportional to the number of monomer units in the molecule. If the molecules were spheres of constant density and susceptible to free radical transfer only on their surfaces, then the probability of branching would be proportional to the number of monomer units raised to the two-thirds power. In general, it could be expected that the probability of branching would be proportional to the molecular weight raised to the α power, where α has a value between two-thirds and one and is probably a function of the number of monomer units in the molecule.

Under these conditions, the weight average degree of polymerization, which is very sensitive to the relatively few molecules in the long high molecular weight "tail" of the distribution curve, would not be expected to increase so rapidly with polymer/monomer ratio as does equation 27. The dotted line in Fig. 4 shows what might be calculated if α were equal to $f(x)$, where $f(x)$ is the correct but unknown function to describe the probability of free radical transfer to a polymer molecule. Different values of $f(x)$ could be chosen empirically to obtain a better fit of the experimental data. However, such calculations cannot give analytical solutions but would involve numerical computations which have not been carried out.

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[Contribution from the Polychemicals Department, E. I. du Pont de Nemours and Company, Inc.]

The Molecular Structure of Polyethylene. V. The Effect of Chain Branching and Molecular Weight on Physical Properties[1]

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It is shown that various properties of polyethylene resins are controlled by combinations of the independent structural parameters of short chain branching, long chain branching and molecular weight. Stiffness, yield point, melting point and sorption of reagents are controlled primarily by crystallinity as affected by short chain branching and measured by density. Ultimate elongation, Vicat temperature and hardness are controlled by both density and melt viscosity (measuring molecular weight). Finally, the viscoelastic properties of the molten polymer and the ultimate strength of the solid are controlled by molecular weight and the amount of long chain branching. Equations representing the relationship between these variables are presented, and an explanation is given for apparent anomalies in the literature.

Introduction

The effect of varying molecular weight and crystallinity on the physical properties of polyethylene has been discussed in general terms by Richards[2] and more recently by Franta.[3] As has been shown in the previous papers of this series,[4,5] total branching (mostly short chain branching) can now be explicitly specified as the primary cause of differences in crystallinity of the solid polymer. Long chain branching and molecular weight are the other major variables of molecular structure.[6,7] This paper will describe, in more detail, the effect of these three independent variables on specific physical and mechanical properties of polyethylene resins.

Experimental

Determination of Physical Properties of the Polymers.—The polymers used in this study were synthesized under a variety of polymerization conditions. The test specimens were prepared by compression molding at 160° followed by cooling in the press. An additional thermal treatment was given some of the specimens, usually involving heating for one hour in boiling water. The properties of polyethylene that will be discussed are listed in Table I together with the ASTM test designation or pertinent information for tests that are not ASTM standards.

These tests were selected to give measures of the molecular structure and of other typical properties of polyethylene resins. The mechanical properties include stiffness (a flexural modulus), hardness and the stress–strain properties in tension. Figure 1 shows the stress–strain relationship for a sample of high molecular weight polyethylene. After the initial, nearly linear deformation the sample passes through the yield point. There is a sharp drop in the tensile stress after the yield point, accompanied by necking down of the test specimen. This is followed by cold drawing with orientation and high elongation. Finally the stress increases to the break point (ultimate strength). Vicat temperature and crystalline melting point illustrate thermal properties. Melt extensibility illustrates visco-

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[1] Presented at the 123rd National Meeting of the American Chemical Society, Los Angeles, Cal., March 16, 1953.

[2] R. B. Richards, *J. Applied Chem.*, **1**, 370 (1951).

[3] W. A. Franta, U. S. Patent 2,586,322.

[4] M. J. Roedel, This Journal, **75**, 6110 (1953).

[5] W. M. D. Bryant, *ibid.*, **75**, 6113 (1953).

[6] F. W. Billmeyer, Jr., *ibid.*, **75**, 6118 (1953).

[7] J. K. Beasley, *ibid.*, **75**, 6123 (1953).