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.

Acknowledgments.—The author gratefully acknowledges the assistance of Professor W. H. Stockmayer of the Massachusetts Institute of Technology and of the other authors of this series in many stimulating discussions covering several phases of this work.

WILMINGTON, DELAWARE

[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]

BY C. A. SPERATI, W. A. FRANTA AND H. W. STARKWEATHER, JR.

RECEIVED APRIL 20, 1953

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).

elastic properties, and cloud point and sorption of reagents illustrate miscellaneous properties.

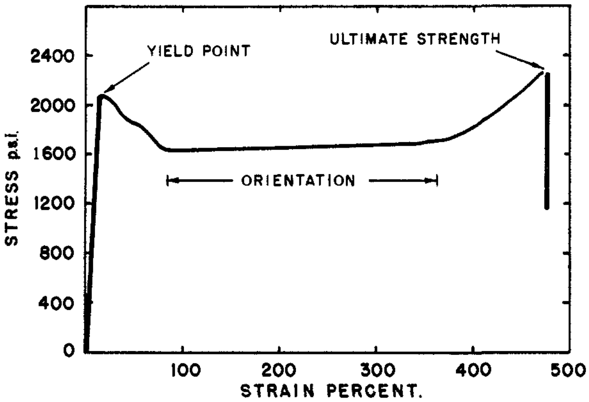

Fig. 1.—Tensile properties of polyethylene.

Determination of Short Chain Branching and Crystallinity.—It has been shown earlier[8] that the density of a given sample of polyethylene correlates well with the per cent. crystallinity of that sample as determined by X-ray diffraction or infrared analysis. Equation 1 in Table II is this relationship between density and crystallinity. Thus, a precise method for determining the density of a polymer provides a rapid, convenient means for estimating its crystallinity. The procedures used to measure density give values reliable at the 95% confidence level to about ±0.0002–0.0004 g./cm.^{3} This is equivalent to a change in crystallinity of ±0.3–0.5%.

Equation 2 expresses density as a function of methyl groups/100 carbon atoms. This linear relationship is suitable for the range shown, but some curvature is needed to express the results at very low amounts of chain branching. We see that total chain branching is the major variable controlling density (and crystallinity). Other factors influencing the crystallinity but of lesser importance are (a) thermal history of the polymer and (b) molecular weight below a certain minimum value.

Determination of Molecular Weight.—Harris[10] observed that the intrinsic viscosity of polyethylene proves to be a good measure of number average molecular weight. Richards[11] presented a similar relationship between melt viscosity and number average molecular weight. We have found that the melt viscosity is directly related to the intrinsic viscosity and thus to the number average molecular weight. There are some anomalies within specific groups of samples, but over a large range Richards'[11] relationship is applicable. Thus either intrinsic viscosity or melt viscosity is a convenient measure of the number average molecular weight. In practice the melt viscosity was generally measured in terms of melt index described by Tordella.[12] Melt index is a fluidity or flow rate and is inversely related to melt viscosity. Since the polymers studied covered a range of molecular weights corresponding to about eight powers of ten in melt index, the melt index of the sample was converted to the logarithm of the melt viscosity in poises at 190°.

TABLE I

TESTS ON POLYETHYLENE

Property	Method
Related to molecular structure	
Crystallinity	X-ray, see ref. 8
Density at 23°	Flotation similar to ref. 9 using KI in aqueous methanol or hydrostatic in C.P. methanol. All samples were molded at 160° and conditioned 24 hr. at 23°
Long chain branching index	See ref. 6
Melt index	ASTM D-1238-52T, see ref. 12
Methyl groups/100 carbons	Infrared analysis, see ref. 5
Mol. wt. (no. av.)	See text and ref. 6, 10 and 11
Mechanical properties	
Hardness	Shore Durometer C Scale
Stiffness (Tinius–Olsen)	ASTM D-747-50
Tensile properties	ASTM D-412-41—Run on Scott or Instron tester usually at 20 in./min.
Yield point (upper yield stress)	
Ultimate strength	
Ultimate elongation	
Thermal properties	
M.p., °C.	Temp. at which crystallinity disappeared between crossed Nicols on a hot stage microscope
Vicat temperature (modified)	Temp. required to give 1 mm. penetration with a 1 sq. mm. needle under a 1-kg. load while temperature is increasing 50°/hr.
Viscoelastic behavior	
Melt extensibility	The ratio of length at break of a section of molten polymer to the original length[a]
Miscellaneous properties	
Cloud point	Temp. of formation of a second phase in a 1% solution of polyethylene in refined paraffin (m.p. 56–57°)
Sorption of reagents	Weight increase (mg.) of specimen 2.0″ × 0.50″ × 0.060″ after immersion in the test reagent for 7 days at 50°. Test reagents were lard and concd. nitric acid

[a] Molten polyethylene is forced through a small rectangular orifice with a shear stress at the wall of about 10^6 dynes/sq. cm. The corresponding rate of shear is about 500 reciprocal seconds, a region in which the material exhibits definite non-Newtonian behavior. The molten polymer is then extended at an increasing rate of elongation until finally the polymer tears. The results are expressed as an elongation ratio, that is, the final length of the molten polymer when it tears divided by the initial length.

Equation 3 relates melt index to the melt viscosity (at 190°) that would be expected at a shear rate of one reciprocal second; in effect, the viscosity at shear rates so low the polymer behaves as a Newtonian fluid. The treatment we used is discussed by Reiner.[13] Equation 4 shows melt index as a function of number average molecular weight determined by the osmotic procedure. The semi-logarithmic relationship used gives the best straight line for the experimental points. Equation 5 is the relationship used by Richards[11] for a much wider range of data than is included in equation 4.

General.—To minimize confusion in the figures, we have plotted only enough points to illustrate the range and trend

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(8) W. M. D. Bryant, J. P. Tordella and R. H. H. Pierce, Jr., "An Investigation of the Crystallinity of Polythene," presented at A.C.S., meeting, Chicago, 1950.

(9) E. Hunter and W. G. Oakes, *Trans. Faraday Soc.*, **41**, 49 (1945).

(10) I. Harris, *J. Polymer Sci.*, **8**, 353 (1952).

(11) F. Bebbington, E. Hunter and R. B. Richards, The Molecular Weight Distribution of Polyethylene, presented at the International Congress, New York, N. Y., September, 1951.

(12) J. P. Tordella, "Tentative Methods of Test for Measuring Flow Rate of Thermoplastics by an Extrusion Plastometer," ASTM Designation D-1238-52T. See also J. P. Tordella and R. E. Jolly, *Modern Plastics*, **31**, no. 3 (October) 146 (1953).

(13) M. Reiner, "Deformation and Flow," H. K. Louis and Co. Ltd., London, 1949, Chapter 6.

TABLE II

QUANTITATIVE RELATIONSHIPS BETWEEN PHYSICAL PROPERTIES

	Relationship	Confidence limits, 95%	r^2	N	Range for which equation is applicable
1	Density = 2.0×10^{-3} (crystallinity) + 0.803	Graphical derivation			Crystallinity from 30 to 85%. Ref. 8
2	Density = $0.9312 - 5.2 \times 10^{-3}$ (CH_3/100 C atoms)	±0.0019	0.87	84	CH_3/100 C from 0.4 to 5.0
3	Log (melt viscosity) = 5.95 − log (melt index)	Graphical derivation			Log melt index from 10^{-3} to 10^{3}
4	Log (melt index) = $5.09 - 1.53 \times 10^{-4} \overline{M}_n$	±1.085	.85	14	$\overline{M}_n$ from 15,000 to 50,000
5	Log (melt viscosity) = $2.74 \times 10^{-2} \sqrt{\overline{M}_n} + 0.64$	±0.269	.98	15	$\overline{M}_n$ from 1800 to 52,000. Ref, 11
6	Log stiffness = 26.420 (density) − 19.889	±0.139	.92	111	Density from 0.900 to 0.940
7	Yield point = 69600 (density) − 62300	±400	.88	169	Density from 0.900 to 0.940
8	Cloud point = 728 (density) − 586	±5	.89	37	Density from 0.900 to 0.940
9	Log (sorption of concn. HNO_3) = 31.07–32.10 (density)	±0.229	.93	8	Density from 0.900 to 0.940
10	Log (sorption of lard) = 47.07–50.18 (density)	±0.357	.93	8	Density from 0.900 to 0.940
11	Log (melt extensibility) = 4.752 − 0.609 log (melt viscosity)	Graphical derivation			Log melt viscosity from 5 to 6
12	Ultimate strength = 346 log (melt viscosity) − 320	±280	.77	96	Log melt viscosity from 3 to 8
13	Vicat temperature = 1382 (density) + 9.29 log (melt viscosity) − 1233	±9	.95	62	Density from 0.91 to 0.94; log melt viscosity from 0 to 7
14	Hardness = 1160 (density) + 2.80 log (melt viscosity) − 1000	±8	.89	37	Density from 0.90 to 0.94; log melt viscosity from 1 to 7

of the data. Whenever possible we have shown the best straight line calculated by the method of least squares. The straight lines represent the data well over the range studied. Refinements, however, may require equations of a different form. For example, reciprocal density rather than density is probably linearly related to crystallinity. As a result, the properties expressed as linear functions of density should be expressed as some reciprocal function. This type of change may explain some of the curvature that must be present if the relationships are to be extrapolated to include polymers at the extremes of crystallinity. Table II is a tabulation of all the equations obtained in this work together with the statistics that show the reliability and limitations of the data.

Discussion

Although interpretation of the effect of molecular structure on some of the properties of polyethylene requires the three-parameter system suggested by Roedel,[6] other mechanical properties of the solid polymer are substantially unaffected by long chain branching. Quantitative correlation of the data can therefore be simplified by using a plane projection of the three-dimensional model. Richards[2] has done this qualitatively in his Fig. 1 by locating various polymers on a plot of crystallinity against molecular weight. This is equivalent to locating any polymer by plotting its density against its log melt viscosity. Such plots will be used to correlate the specific properties with the molecular structure of polyethylene.

Properties Related to Density. A. Stiffness and Yield Point.—Figure 2 shows that the stiffness of various polyethylenes is dependent primarily upon the crystallinity of the sample as measured by the density. The lines shown connect points of equal stiffness. Such lines which connect points having the same value of a property are termed isopleths. The range of viscosities was ten million-fold and the densities covered represent crystallinity from 40 to 80%. It is desirable to re-emphasize this observation that at constant density the stiffness is independent of melt viscosity. Since these isopleths are all parallel to the viscosity axis, a function of

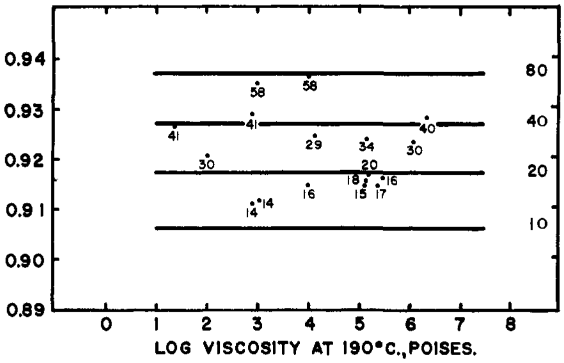

Fig. 2.—Stiffness × 10^{-3} p.s.i.

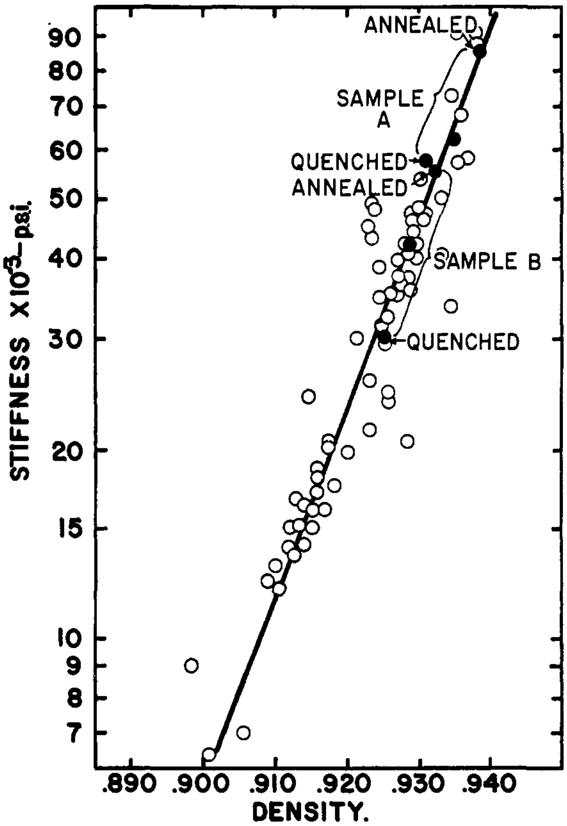

Fig. 3.—Log stiffness *vs.* density and effect of thermal treatment on stiffness.

stiffness can be plotted against density alone to obtain the relationship shown in Fig. 3. This plot shows a good correlation (expressed in equation 6), but it also shows a considerable scatter of points. The scatter emphasizes the fact that many of the mechanical properties are controlled both by the molecular structure and by the way the particular test specimen was made. The effect of thermal history on the stiffness of two different polyethylenes is shown by the solid points on Fig. 3. The fact that crystallinity is influenced by thermal treatment as well as by short chain branching was mentioned earlier. Here the logarithm of the stiffness of the sample is plotted against the density for test speciments that were cooled very slowly, normally and very rapidly. The changes are compared to the reference line. The value for density of these points is not the "standard density" used in all of the other relationships but is the actual density of the test specimen. It is apparent that the changes in stiffness or density resulting from thermal treatment of a particular sample, while important, involve only a small part of the total range observed with polyethylenes.

Since yield point plotted against density and melt viscosity also shows isopleths parallel to the abscissa, it is plotted as a function of density alone (Fig. 4 and equation 7). The solid points and broken line show the greatly decreased scatter of points observed when rigorously controlled conditions are used for preparing and testing the samples, as contrasted to normally good technique among a group of technicians. In this set of data, the test specimen received no additional thermal treatment, and thus the line falls below the relationship that includes many annealed samples.

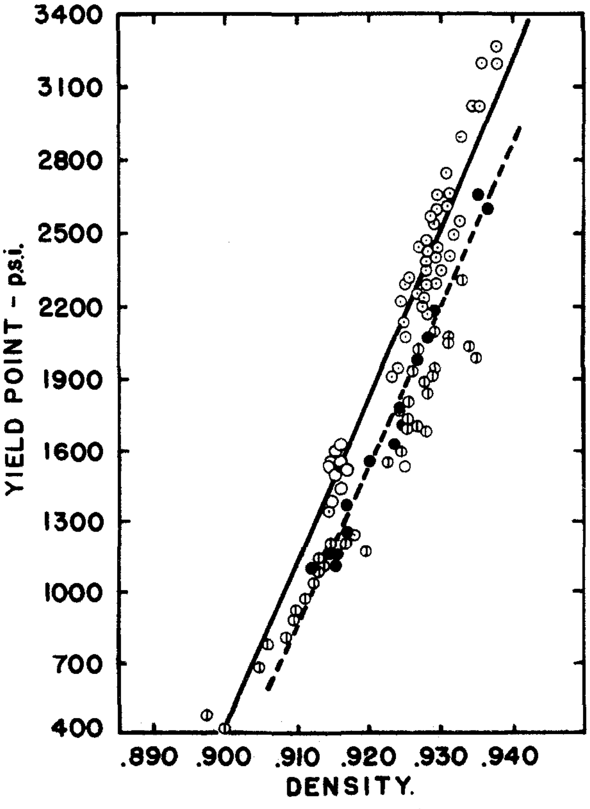

Fig. 4.—Yield point *vs.* density.

B. Melting Point, Cloud Point and Sorption of Reagents.—Not only does the crystallinity alone control many of the mechanical properties of polyethylene, but it also affects such properties as the crystalline melting point, the cloud point and the sorption of reagents. The quantitative relationships are shown in Figs. 5 and 6 and equations 8, 9 and 10. As in the earlier examples, these data were obtained on polymers having a wide range of molecular weights. These properties, like yield

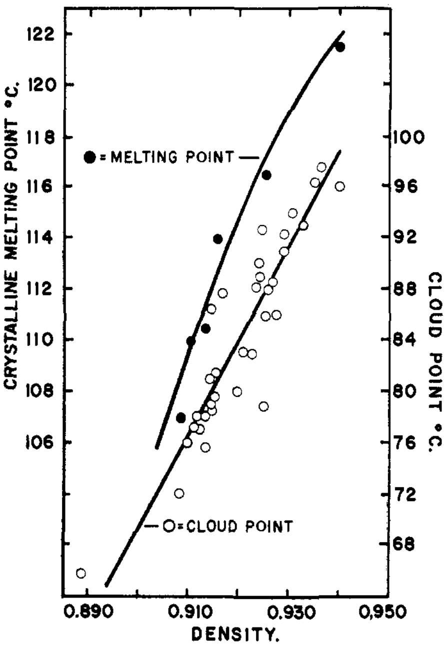

Fig. 5.—Crystalline melting point and cloud point *vs.* density.

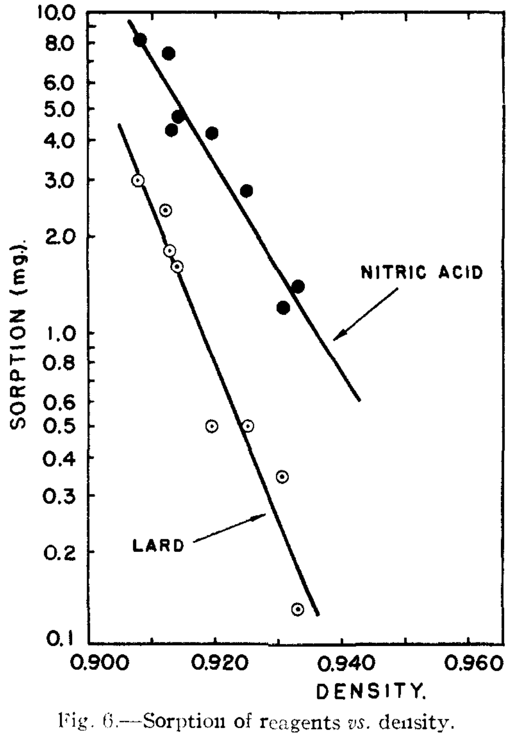

Fig. 6.—Sorption of reagents *vs.* density.

point and stiffness, are independent of molecular weight.

The Effect of Distribution of Short Chain Branching.—The data in Table III show that short chain branching need not be distributed evenly within all the polymer chains, but that an average branching is the effective factor. Thus, substantially the same values are obtained for a polymer of intermediate crystallinity obtained by blending polymer of high and low crystallinity as are observed from a material of similar crystallinity obtained by direct synthesis. Sample B was so brittle and fragile that it was not possible to measure its stiffness or yield point.

TABLE III

THE EFFECT OF DISTRIBUTION OF SHORT CHAIN BRANCHING

Sample	Log viscosity	Density		Yield point		Stiffness	
		Predicted	Measured	Predicted	Measured	Predicted	Measured
A	7.4	....	0.9143	..	1290	....	16,900
Blend of A and B (55.5% A)	5.5	0.9254	.9260	1750	1770	38,000	39,600
B	2.4	....	.9397	..	..	....	....

Anomalies from the Literature.—We have just seen that many properties of polyethylene are independent of molecular weight over a very large range of molecular weights and are dependent only upon crystallinity. This conclusion is apparently at odds with various reports in the literature.[14-16] The discrepancy results from the fact that in a series of polyethylenes of increasing molecular weight made under similar conditions, a decrease in chain branching with the resulting increase in stiffness is observed. This increase, though, results from the fact that the chain branching has been decreased during polymerization independent of but concurrent with the increase in molecular weight. However, as we saw earlier, if the molecular weight is changed while maintaining the same level of branching (density), there is no change in stiffness. Similar fallacies have been published for most of the other properties which are dependent upon the amount of short chain branching in the polymer.

Properties Related to Viscosity and Long Chain Branching. A. Viscoelastic Behavior.—The effect of long chain branches on density of the solid polymer is negligible since there are so few present in comparison with the short branches. The long chains can enter the crystalline structure of the solid as readily as can the main chain and the only point of disruption of the order is at the junction with the main chain. On the other hand, long chain branching has a very marked effect on the viscoelastic properties of the melt. This effect may be contrasted to that from short chain branching which has a negligible effect on the properties of molten polyethylene. (The short branches have their primary effect on crystallinity, which in turn is lost at the melting point of the polymer.)

Qualitatively we would expect that molecular entanglement resulting from extensive long chain branching should be particularly effective in increasing the elastic components of the melt. In an attempt to obtain a quantitative picture of the fundamental rheological properties, a test for extensibility of molten polyethylene was devised (see Table I). This test clearly shows these effects of viscosity and long chain branching.

Melt extensibility is a ratio of elongations; the higher this ratio, the greater the extensibility of the melt. Equation 11 shows the decrease in extensibility with increasing molecular weight (melt viscosity) observed for a large number of samples examined in this test. It was found that a series of four closely related polymers with increasing amounts of long chain branching did not fit this line. Figure 7 shows the marked decrease of melt extensibility with increasing long chain branching index.

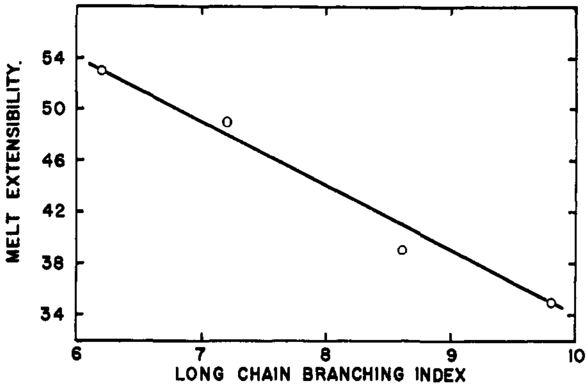

Fig. 7.—Effect of long chain branching on melt extensibility corrected to log melt viscosity = 5.5.

To put these four samples on a common basis in Fig. 7, all of the values for melt extensibility have been corrected to a log viscosity of 5.5 using the rate of change of extensibility with viscosity obtained from equation 11.

Certainly, other factors than these are involved in viscoelastic properties of molten polyethylene. Fundamental information on the spectrum of relaxation times of the molten polymer, for example, should be most illuminating. However, the two parameters of melt viscosity and long chain branching account for a large portion of the differences among samples.

B. Ultimate Strength of Polyethylene.—True values for ultimate strength of low viscosity polyethylene are often difficult to determine in a way

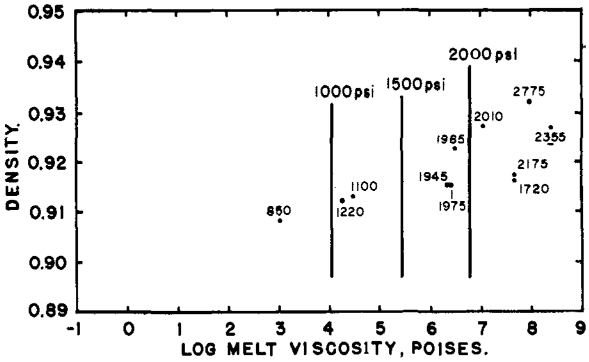

Fig. 8.—Ultimate strength, p.s.i.

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(14) H. F. Robertson, *India Rubber World*, **127**, 80 (1952).

(15) R. H. Carey, E. F. Schulz and G. J. Dienes, *Ind. Eng. Chem.*, **42**, 842 (1950).

(16) F. M. Rugg, J. J. Smith and L. H. Wartman, *J. Polymer Sci.*, **11**, 1 (1953).

comparable to those for high molecular weight polymers. This is true because the sample breaks at the yield point prior to the initiation of cold drawing. Thus significant data are limited to a somewhat narrower range of melt viscosities than are the data on most other mechanical properties. The vertical isopleths in Fig. 8 show that ultimate strength is substantially independent of the density (crystallinity) and is primarily dependent upon the viscosity of the polymer.

Equation 12 shows the calculated relationship over a range of about 100,000-fold in melt viscosity. The samples with extensive long chain branching discussed above also failed to fit equation 12. Figure 9 shows that the ultimate strength of these samples decreases with increasing long chain branching. It follows that in order to characterize polyethylene for properties such as ultimate strength and the viscoelastic properties of the molten polymer, it is necessary to include the third axis of long chain branching in the wedge shaped model discussed by Roedel.[4]

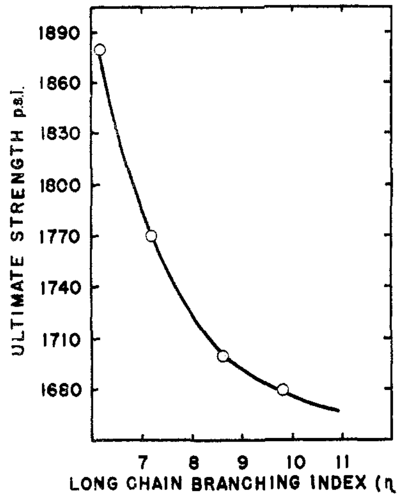

Fig. 9.—Ultimate strength *vs.* long chain branching index.

Properties Related to Viscosity and Density. A. Ultimate Elongation.—The influence of density, viscosity and long chain branching on the yield point and ultimate strength of polyethylene has already been discussed. The factors affecting the ultimate elongation are shown on Fig. 10. The diagonal isopleths show the simultaneous dependence on both density and viscosity. The decreasing elongation with increasing density is related to a considerable extent to the rate of elongation of the specimen as well as the sample size. If the sample is very thin or if it is elongated very slowly, the cold drawing proceeds more readily and very high elongations are often obtained with the highly crystalline polymers.[17] All of the samples shown here were tested at the standard rate of 20 in./min. Although an effect of long chain branching on elongation was not seen within the range of polymers reported here, decrease in elongation with increasing number of long branches has been noted in extreme cases.[4]

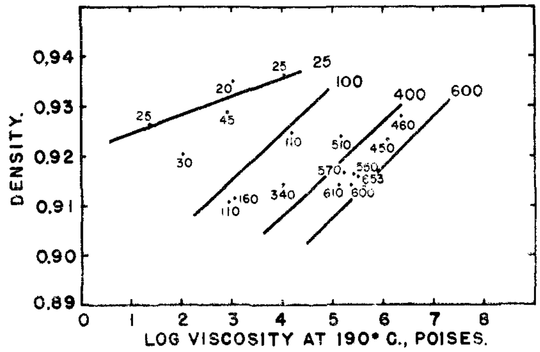

Fig. 10.—Ultimate elongation, %.

B. Vicat Temperature and Hardness.—The diagonal isopleths in Figs. 11 and 12 show the dependence of the modified Vicat temperature and Shore Durometer hardness on both density and melt viscosity. The data for each property were treated in a multiple correlation to give equations 13 and 14. The coefficient of determination of 0.95 for Vicat temperature, for example, shows the excellent correlation.

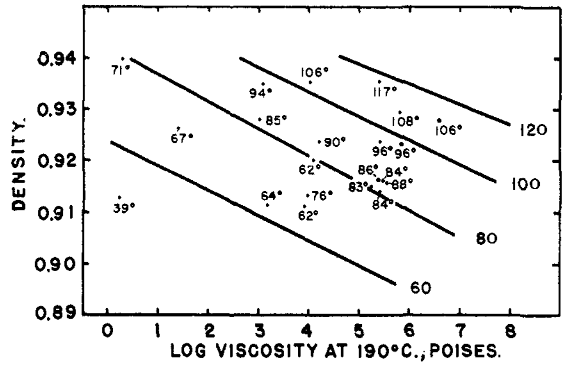

Fig. 11.—Vicat temperature, °C.

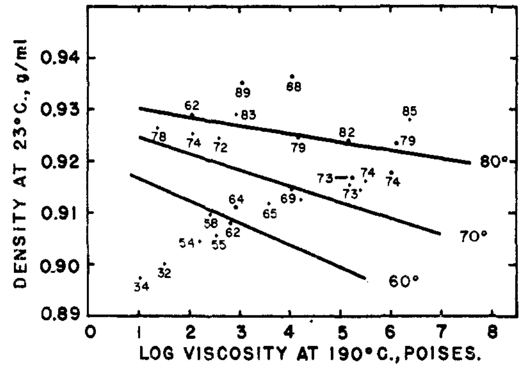

Fig. 12.—Hardness, Shore C.

Theoretical.—A detailed theoretical understanding is not at hand to explain the effect of the molecular structure on the physical and mechanical properties that have been discussed. It is known that a single molecule of polyethylene probably participates in several crystallites.[17] Therefore, we expect to find and do find that properties involving small deformations (usually less than 10%) are dependent primarily on crystallinity and are relatively independent of molecular weight or long chain branching. Conversely, the properties involving large deformations such as ultimate

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(17) W. M. D. Bryant. *J. Polymer Sci.*, **2**, 547 (1947).

strength and behavior of the melts are particularly sensitive to molecular weight and long chain branching.

It now is apparent that many of the differences in behavior of various samples of polyethylene previously attributed to differences in molecular weight distribution are in fact due to differences in short and long chain branching. Nevertheless, there are still unexplained deviations from smooth relationships in the data that have been presented. We feel it is probably due to a combination of the difference in the distribution of molecular weight and long chain branching together with differences in the structure of the crystalline portions of the polymer.[18] Acquiring the understanding needed to explain these apparent anomalies is important. Certainly, as Bryant[17] and Richards[2] have pointed out, the arrangement of the crystalline zones in polyethylene can produce pronounced changes in properties.

In spite of these uncertainties, the significance of the results discussed in this paper extends well beyond the properties of polyethylene. The changes observed in many of the important physical properties due to crystallinity alone, independent of molecular weight, suggest that many of the traditional ideas for the dependence of properties on molecular weight must be revised.

In conclusion, a consistent picture has been presented of the relationships between the molecular structure of polyethylene and various physical and mechanical properties A large portion of the differences between samples is explained by the variation in three independent factors that characterize any sample of polyethylene: namely, the number average molecular weight, the amount of short chain branching and the extent of long chain branching.

Acknowledgment.—The authors wish to express their appreciation to the many individuals in our laboratory who have contributed to this paper: to R. E. Jolly, J. P. Tordella, V. P. Caracciolo and A. E. Symonds who supplied much of the data; to Miss M. T. Dunleavy who performed all of the statistical analyses and especially to D. E. Strain for helpful discussions, guidance and support of all the work discussed in this series of papers.

WILMINGTON, DELAWARE

[18] F. M. Rugg, J. J. Smith and J. V. Atkinson, *J. Polymer Sci.*, **9**, 579 (1952).

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Chain Transfer in the Polymerization of Styrene. VIII. Chain Transfer with Bromobenzene and Mechanism of Thermal Initiation[1]

BY FRANK R. MAYO

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The rate and degree of the thermal polymerization of styrene have been studied at 60, 155 and 176° in bromobenzene as solvent, with styrene concentrations from 7.6 to 0.05 *M*. Low molecular weight, saturated, probably cyclic material and higner molecular weight, unsaturated polystyrene seem to be formed in independent reactions, and have been partially separated by precipitation of the higher polymer with methanol. Data on boiling points and unsaturation of dimer and trimer fractions are presented. The low molecular weight saturated polymer results from a non-radical or a biradical reaction, and the saturated dimer is thought to be a diphenylcyclobutane. The high polymer results from an over-all $^5/_2$-order reaction which requires a termolecular reaction of styrene to give two monoradicals, a conclusion consistent with the observed activation energies. There is now no evidence for, and considerable evidence against, any participation of biradicals in the formation of high polymer from styrene. Bromobenzene has about the same reactivity as benzene and chlorobenzene in chain transfer, as measured by the molecular weight of the polystyrene formed. Nevertheless, no significant quantities of bromobenzene are incorporated in the polymer. It is concluded that certain aromatic solvents participate in the chain transfer reaction without permanently combining with the polymer, the net result being chain transfer with the monomer. Two mechanisms for this process are proposed which correlate observations in other polymer and non-polymer reactions.

Previous papers in this series[2] have shown that effects of solvents in decreasing molecular weight in the thermal polymerization of styrene are satisfactorily accounted for by chain transfer with the solvent, at styrene concentrations as low as 0.4–0.6 *M* in cyclohexane, benzene and ethylbenzene and 0.14 *M* in toluene.[3,2a,2c] In the presence of carbon tetrachloride,[2b] carbon tetrabromide,[4] or mercaptans,[2e] the molecular weights of the polymers depend in the same manner on the monomer–solvent ratio, and contain one solvent molecule per polymer molecule. The isolation in good yields and proof of structure of 1:1 products from styrene and carbon tetrabromide or bromotrichloromethane leave no doubt as to the mechanism of chain transfer with these solvents.[5] Further, in every case examined above, the over-all second-order rate constants were nearly independent of monomer concentration and of solvent

However, a single experiment by Breiten-

[1] A preliminary account of this work was presented at the Symposium on Refinements in Polymerization Kinetics at the Buffalo Meeting of the American Chemical Society, March 25, 1952.

[2] (a) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943); (b) R. A. Gregg and F. R. Mayo, *ibid.*, **70**, 2373 (1948); (c) R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947); (d) F. R. Mayo, THIS JOURNAL, **70**, 3689 (1948); (e) R. A. Gregg, D. M. Alderman and F. R. Mayo, *ibid.*, **70**, 3740 (1948); (f) F. R. Mayo, R. A. Gregg and M. S. Matheson, *ibid.*, **73**, 1691 (1951); and (g) R. A. Gregg and F. R. Mayo, *ibid.*, **75**, 3530 (1953).

[3] (a) H. Suess, K. Pilch and H. Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937); (b) H. Suess and A. Springer, *ibid.*, **A181**, 81 (1937); (c) G. V. Schulz, A. Dinglinger and E. Husemann, *ibid.*, **B43**, 385 (1939).

[4] C. H. Bamford and M. J. S. Dewar, *Disc. Faraday Soc.*, **2**, 314 (1947).

[5] M. S. Kharasch, E. V. Jensen and W. H. Urry, THIS JOURNAL, **69**, 1100 (1947); M. S. Kharasch, O. Reinmuth and W. H. Urry, *ibid.*, **69**, 1105 (1947).