turbance, and hence with a smaller, positive entropy of activation. Further, since the activated complex for the diffusion of zinc ion may become more hydrated, the E_{act} for this ion will also be lowered.

The extension of this interpretation to the diffusion of ions present in trace quantities in otherwise homo-ionic exchanger salts does not seem feasible until the results from additional quantitative measurements are available.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY]

The Molecular Structure of Polyethylene. I. Chain Branching in Polyethylene during Polymerization[1]

BY M. J. ROEDEL

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Two types of branching can occur during the free radical polymerization of ethylene. These two types depend upon different polymerization variables and affect different physical properties of the formed polymer. Long chain branching is due to intermolecular hydrogen transfer, is dependent upon polymer concentration, and mainly affects rheological properties. Short chain branching is believed to be due to intramolecular hydrogen transfer *via* transient ring formation, is dependent upon polymerization temperature, and mainly affects properties in the crystalline state.

Introduction

The first suggestion of branching in vinyl polymers was made by Staudinger and Schulz[2] in 1935 after observing discrepancies between osmotic and viscosity molecular weights for polystyrenes prepared over a wide temperature range. This was confirmed by Alfrey, Bartovics and Mark[3] in 1943. In 1937 Burk[4] speculated that free radical polymerization should lead to extensive branching. Flory[5] suggested branching by intermolecular hydrogen transfer, first in 1937 and again in 1947. Fox and Martin[6] in 1940 stated that the infrared analysis of polyethylene indicated a high degree of branching with the proportion of methyl groups varying between 1 CH_3 per 8 CH_2 for a low molecular weight fraction to 1 CH_3 per 100 CH_2 for a high molecular weight fraction. They also suggested that the presence of these methyl groups might confer special properties on the polyethylene. Roland and Richards[7] recently have discussed branching *via* grafting polyethylene to polyvinyl acetate.

In the early 1940's during the course of research on the high pressure polymerization of ethylene, following the original discovery by Fawcett, Gibson and Perrin,[8] it became apparent that marked differences in physical properties exist among polyethylenes polymerized under different synthesis conditions. These differences are of considerable magnitude in many basic physical properties such as density, crystalline melting point, Young's bending modulus, tensile strength and vapor permeability. Furthermore, these differences are relatively independent of the viscosity molecular weight over a considerable range. This phenomenon was attributed by some to molecular weight distribution and by others to branching by the intermolecular hydrogen transfer process suggested by Flory.[5]

Fractionation studies to determine the molecular weight distribution were complicated by the insolubility of polyethylene at ordinary temperatures. Also, we felt that if branching existed, fractionation would give a molecular weight distribution complicated by a branching distribution. Since the Flory branching mechanism would be directly dependent upon the polymer concentration during synthesis, this variable was studied with respect to its effect on the physical properties of the resulting polymers.

Results

Research was carried out in high-pressure polymerization equipment using a peroxide catalyst in a solvent medium. Synthesis conditions included constant temperature and pressure with variable polymerization time in order to vary the polymer concentration. Table I lists the data obtained from two polyethylene runs carried out at low and at high polymer concentration.

TABLE I

EFFECT OF POLYMER CONCENTRATION

Final monomer/polymer ratio[a]	Inh. visc.[b]	Tensile prop. p.s.i./% elong.	Melt flow rate[c]	Melt flow temp.,[d] °C.	Insoluble fraction
94/6	0.79	2980/625	1.29	138	Low
13/87	1.06	1590/240	0.09	>250	High

[a] See Example 1 of U. S. Patent 2,409,996 for one method of experimental operation. [b] Determined on a 0.125% solution of polyethylene in xylene at 85°. [c] The number of grams extruded in a 10-minute interval through a $^1/_{16}$ inch orifice at 190° under 25 p.s.i. nitrogen. [d] Temperature at which sample flowed out under its own weight wetting the melting point block. > 250° indicates the sample was elastic up to the decomposition temperature.

The data in Table I indicate that at least one of the samples is not linear in structure because, *a priori*, for a linear polymer structure the tensile

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

(2) H. Staudinger and G. V. Schulz, *Ber.*, **68**, 2320 (1935).

(3) T. Alfrey, A. Bartovics and H. Mark, THIS JOURNAL, **65**, 2319 (1943).

(4) R. E. Burk, H. E. Thompson, A. J. Weith and I. Williams, "Polymerization," A. C. S. Monograph Series, Reinhold Publ. Corp., New York, N. Y., 1937, p. 140.

(5) P. J. Flory, THIS JOURNAL, **59**, 241 (1937); **69**, 2893 (1947).

(6) J. J. Fox and A. E. Martin, *Proc. Royal Soc.* (*London*), **A175**, 226 (1940).

(7) J. R. Roland and L. M. Richards, *J. Polymer Sci.*, **9**, 61 (1952).

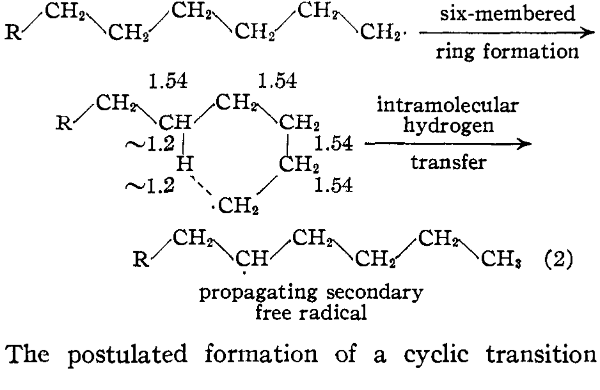
(8) E. W. Fawcett, R. D. Gibson and M. W. Perrin, U. S. Patent 2,153,553.

strength should be inversely proportional to the melt flow rate, since both are molecular weight dependent. Since the sample prepared at high polymer concentration during synthesis is not only weaker in tensile strength properties but also is more elastic in the melt and contained a higher proportion of insoluble material, it appears to possess the more highly branched structure in accordance with Flory's intermolecular hydrogen transfer mechanism

$$\underset{\text{propagating chain}}{R_1CH_2CH_2\cdot} + \underset{\text{dead polymer molecule}}{R_2CH_2CH_2R_3} \xrightarrow[\text{hydrogen transfer}]{\text{inter-molecular}} \underset{\text{dead polymer molecule}}{R_1CH_2CH_3} + \underset{\text{propagating chain}}{R_2\dot{C}HCH_2R_3} \quad (1)$$

By this mechanism the polyethylene molecule that is reactivated by hydrogen transfer propagates a long side branch from the transfer site until it in turn is terminated by chain transfer with another molecule or by mutual termination with another free radical. The data indicate that the first molecules formed give rise to a high polymer than can be cold drawn some 600% and which forms a relatively fluid melt at 138°. However, as polymerization proceeds the original polyethylene becomes more highly branched with long side chains due to reactivation by hydrogen transfer and the tensile properties decrease despite an increase in the viscosity molecular weight. At the same time the melt becomes more elastic in character along with the formation of numerous insoluble particles consisting of molecules containing many branches.

Short Chain Branching.—Despite the marked differences in tensile properties and melt characteristics between the above two described polyethylenes their crystalline behavior with respect to density, stiffness, melting point and moisture permeability were found to be practically identical. These latter physical properties, however, could be varied by varying the temperature of polymerization. Since these latter property variations are independent of polymer concentration a second branching mechanism must be operating by an intramolecular process. We propose that this second branching mechanism is due to an intramolecular hydrogen transfer reaction occurring *via* transient 5- or 6-membered ring formation.



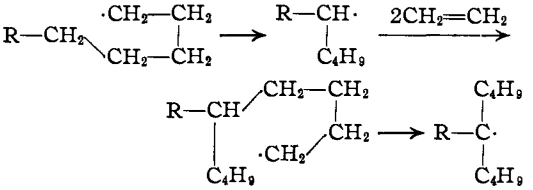
(2)

propagating secondary
free radical

The postulated formation of a cyclic transition state of the Eyring–Gorin type[9] is an important feature of this mechanism. Probable bond lengths in ångström units for the transition state are shown. Study of a Hirshfelder model indicates that C_4 branches should be most probable followed by C_5 and C_3. After addition of one ethylene molecule to the secondary free radical, the latter becomes a primary free radical. Propagation continues with interruption every so often, depending upon the temperature and ethylene concentration, by the short chain branching mechanism.

If Flory's long chain branching mechanism is accepted as correct, then the short chain branching mechanism must be accepted as very probable, since the latter is favored both sterically and by the high polymer "concentration" within a five carbon radius of the propagating radical. The data bear this out since the density can be varied from about 0.89 to 0.97 g./ml. by variation of polymerization temperature between wide limits, whereas the effects of polymer concentration on density can scarcely be detected. Therefore, the intramolecular hydrogen transfer mechanism is the major branching mechanism in polyethylene with respect to number of branch sites.

It appears probable that two short chains can originate from the same carbon atom. This results from a repetition of the short chain branching mechanism on the same carbon atom after addition of two more ethylene molecules to the secondary free radical. This process gives rise to a tertiary free radical before propagation continues



(3)

Thus in a very short interval of time a single carbon atom may exist as three distinctly different free radical entities—primary, secondary and tertiary alkyl.

The mechanism of short chain branching is thermodynamically favorable, judging by trends in free radical reactions uncovered by Bryant.[10] The following equation for the chain transfer step assumes, for lack of better information, that the secondary dodecyl radical is related to the primary dodecyl radical in the same manner as isopropyl is to *n*-propyl

$$n\text{-}C_{12}H_{25}\cdot(g) = n\text{-}C_7H_{15}—\dot{C}H—C_4H_9\text{-}n\ (g);$$
$$\Delta H_{298.16} = -6.0\ \text{kcal.}\quad \Delta F^\circ_{298.16} = -6.3\ \text{kcal.} \quad (4)$$

A similar equation based on the differences between tertiary and *n*-butyl radicals takes care of the formation of a tertiary radical

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(9) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 135, 257.

(10) (a) W. M. D. Bryant, *J. Polymer Sci.*, **6**, 359 (1951), especially page 368; (b) private communication. The free energy data have been revised to conform to a non-planar arrangement of groups about the trivalent carbon atom. This results in a decrease in the free energy of formation of 0.4 kcal. for radicals having a symmetry number greater than unity for the planar arrangement. Values for unsymmetrical structures are unchanged.

$$n\text{-}C_6H_{13}CH(CH_3)C_4H_8\cdot(g) = n\text{-}C_6H_{13}\dot{C}(CH_3)C_4H_9n\ (g)$$
$$\Delta H_{298\cdot16} = -9.6\text{ kcal.};\ \Delta F^\circ_{298\cdot16} = -8.3\text{ kcal.} \quad (5)$$

Equation 5 represents the case of short chain branching on a carbon atom already having one branch. Although somewhat more favorable thermodynamically, the steric requirements are more severe, hence the relative importance of this mechanism is difficult to assess. The next equation shows that the propagation reaction, also applicable to the *growth* of a branch, is favorable

$$n\text{-}C_{10}H_{21}\cdot(g) + C_2H_4(g) = n\text{-}C_{12}H_{25}\cdot(g)$$
$$H_{298\cdot16} = -22.4\text{ kcal.};\ \Delta F^\circ_{298\cdot16} = -12.2\text{ kcal.} \quad (6)$$

The same type of equation would hold for the *initiation* of branching, but the result would be slightly less favorable since the reacting radical would be of the more stable secondary or tertiary type. Energetic properties in the paraffin hydrocarbon series assume a constant increment per CH_2 group above about six or seven carbon atoms[10]; hence the behavior of dodecyl radicals should typify that of the growing polyethylene chains also.

It was stated above that short chain branching is essentially independent of polymer concentration, but strongly influenced by the temperature of polymerization. The latter feature is probably not a result of the free energy change, which, for the transfer steps (equations 4 and 5), would be favorable over the whole range of polymerization temperature. It is believed that the moderately large activation energies of 7–8 kcal. associated with chain transfer reactions[11] of the type in question, compared with the small activation energy of 2–3 kcal. for propagation[12] are responsible for the increased branching at higher temperatures.

It also appears probable that both short chain and long chain branching can occur in other vinyl, vinylidene and diene polymerizations just as in ethylene polymerization. Particularly in diene polymerization intramolecular chain transfer might be pronounced because of the presence of active allylic hydrogen and addition across the double bond when sterically favorable. Similar branching mechanisms may exist during ionic polymerization, and the degree of branching should depend not only on the particular monomer used but also on whether anionic or cationic catalysis is involved.

It also appears likely that a third type of branching can occur involving intramolecular hydrogen transfer further back than 6-membered ring[13] formation. A minor amount of long chain branching may also occur by copolymerization through polymer unsaturation arising from chain termination *via* disproportionation or chain transfer with monomer. It is unlikely that long chain branching can occur without its concomitant short chain branches whereas it is possible for short chain branches to be formed with practically no long chain branches present.

The long chain branching process can lead to a very wide molecular weight distribution. The short chain branching process has no direct effect on molecular weight distribution, since no interchange transfer is involved. Short chain branching does, however, have an indirect effect on molecular weight distribution in that a polyethylene molecule containing tertiary hydrogen atoms is more susceptible to free radical attack than one containing only secondary hydrogen atoms.

Effect of Branching on Physical Properties.—The effect of branching on physical properties is very pronounced as might be expected for a polymer where density of laboratory samples can be varied about 10% by using a wide range of polymerization conditions. Since most of the branch sites are from short chains, this type of branching has the most marked effect on those properties affected by the crystallinity of the polymer such as melting point, yield point, bending modulus, hardness and vapor permeability. Long chain branching, while it has a relatively minor effect on crystallinity because of its low number average, has a marked effect on melt flow and viscoelastic properties. Thus, to describe fully the physical properties of any particular sample of polyethylene a minimum of at least three parameters is required: the average molecular weight, the degree of short chain branching and the degree of long chain branching. Because of these three independent parameters of molecular structure, products can be synthesized ranging from waxes to tough plastics by control of molecular weight, from flexible to stiff polymers by control of short chain branching, and from plastic to elastic melts by control of long chain branching. The effects of molecular weight distribution and branching distribution on the physical properties of polyethylene have not yet been defined fully.

Succeeding papers in this series will discuss methods that have been developed to measure quantitatively both short and long chain branching content in polyethylene, a kinetic treatment of branching, and detailed characterization of polyethylene *versus* branching content. These data indicate that on a number average basis no more than about one long chain branch per molecule can be present and the ratio of short chain branches to long chain branches can be as high as 50 to 1.

WILMINGTON, DELAWARE

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[11] A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

[12] For example, H. W. Melville and J. C. Robb, *Proc. Roy. Soc.* (*London*), **202A**, 198 (1950).

[13] A similar "backbiting" mechanism proposed by G. W. King involving formation of C_8–C_{18} side chains by intramolecular hydrogen transfer is discussed in the recently published book "Styrene—Its Polymers, Copolymers and Derivatives" by R. H. Boundy and R. F. Boyer, A. C. S. Monograph Series No. 115, Reinhold Publ. Corp., New York, N. Y., 1952, p. 231.