equatorial beta hydrogens, with further splittings by either alpha or gamma hydrogens. The corresponding non-bridged structure would give a basic five line pattern instead of three.

Propylene and Ethylene + HBr.—The spectra obtained for the ultraviolet irradiated ethylene and propylene plus hydrogen bromide, dissolved in pentane were observed to develop very rapidly. Measurable signals were obtained in less than one minute. The spectra appear to be characteristic of a single line anisotropically broadened. Attempts were made to operate at higher temperatures in hopes of improving resolution, but the radicals were too unstable. No interpretation of the spectra is offered.

Experiments with DBr.—Spectra were obtained for 2-butene and cyclopentene plus deuterium bromide, photolyzed at 77°K. These spectra were identical with the spectra obtained with hydrogen bromide. Consequently the same bromoalkyl radical intermediate is formed with both HBr and DBr indicating the Br adds first. It was observed that in every case when deuterium bromide was the source of the bromine atom that the growth of the signal was much slower than with HBr. There may well be some connection here between the isotope effect observed by Goering and Larsen[6] and the slower radical formation observed here.

Although one cannot arrive at an unequivocable conclusion that these electron paramagnetic resonance results definitely establish a bridged intermediate in the hydrogen bromide addition to olefins, it is certainly true that the consistency of the bridged structure in fitting the observed spectra suggest the probability of such a mechanism. It must be pointed out, however, that the bridged structure does not imply a fixed or static structure, but the bridge can be looked upon as resulting from a resonating structure in which the Br atom oscillates between carbons at a frequency greater than or equal to the magnitude of the hyperfine interaction $= 5.0 \times 10^7$ c.p.s. Such an oscillating scheme would yield the same symmetrical spectra observed. In addition, the following points now have been well established; that the bromine atom addition is the initial event in the sequence of addition and that the extreme rapidity of the reaction in the solid, glassy phase has been demonstrated. It is equally obvious that much work yet remains to be done, including extensive studies with deuterium substituted olefins. Such experiments are being planned.

Acknowledgments.—Thanks are due Miss Kathleen Doyle for her assistance in preparation and gas chromatography of a number of the olefins, and to Prof. P. S. Skell for his discussions and suggestion of the oscillating Br atom type structure.

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Transition Metal Catalysts. IX. Random Ethylene–Propylene Copolymers with a Low Pressure Polymerization Catalyst

BY GEORGE W. PHILLIPS AND WAYNE L. CARRICK

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Ethylene–propylene copolymers were prepared at atmospheric pressure with the VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$, hydrocarbon-soluble, polymerization catalyst. A controlled rate of initiation and thus a constant comonomer composition were obtained by the introduction of a constant amount of oxygen into the monomer stream. Three copolymers, containing 2.6, 3.8 and 10 mole % propylene, were found to have uniform comonomer compositions when fractionated by successive extraction with boiling solvents, in contrast to copolymers prepared with other reported Ziegler-type catalysts. An elution fractionation of the 10 mole % propylene copolymer was conducted with cellosolve–xylene mixtures above the copolymer melting point. The molecular weight distribution was shown to approximate the "most probable" distribution. This is in agreement with a previously proposed polymerization mechanism. The propylene contents of each of the fractions from the 10% copolymer were within ±1% propylene of the value of the whole copolymer. This narrow composition distribution is in accord with the statistical distribution predicted theoretically for random copolymers and is in accord with the previous finding that $r_1 \cdot r_2 \cong 1$. These data suggest that Ziegler-type catalysts containing a single active species are amenable to the same statistical and kinetic treatment that has been used for the classical polymerization catalysts.

Introduction

In the copolymerization of two vinyl monomers, there are four separate propagation reactions[1]

$$\begin{aligned} M_1^* + M_1 &\xrightarrow{k_{11}} M_1^* \\ M_1^* + M_2 &\xrightarrow{k_{12}} M_2^* \\ M_2^* + M_2 &\xrightarrow{k_{22}} M_2^* \\ M_2^* + M_1 &\xrightarrow{k_{21}} M_1^* \end{aligned} \qquad (1)$$

where M_1 and M_2 are the two monomers and M_1^* and M_2^* are the growing polymer chain ends terminated by M_1 and M_2, respectively. The reactivity ratio, r_1, is defined as k_{11}/k_{12} and r_2 as k_{22}/k_{21}. When $r_1 \cdot r_2 = 1$, the above equations predict that the resulting copolymer should contain a random distribution of the two monomer units along the polymer chains. Stockmayer[2] has given an extensive statistical treatment of copolymer composition distributions and has concluded that when $r_1 \cdot r_2 \sim 1$ and the degree of polymerization is high, compositional variations between polymer molecules should be quite small with the result that the gross copolymer would be very homogeneous.

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[1] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, Chapter V.

[2] (a) W. H. Stockmayer, *J. Chem. Phys.*, **13**, 199 (1945). (b) R. Simha and H. Branson, *ibid.*, **12**, 253 (1944).

Several studies of olefin copolymerization by organometallic mixed catalysts have been reported recently.[3–7] In all cases the product of r_1 and r_2 approximates unity, but in some instances fractionation of the gross copolymer revealed a much broader composition distribution than that predicted by Stockmayer.[2] Some workers[8–10] have proposed that many of the organometallic mixed catalysts contain more than one active site. One possible interpretation of the observed broad composition distribution is that the catalysts contain many sites with $r_1 \cdot r_2 = 1$ for each site, but with the specific values of r_1 and r_2 differing from site to site. A natural consequence of this argument is the prediction that use of a catalyst containing only one active site should give results that fit the statistical treatment. There is considerable evidence that the soluble, VX_n–$Sn(C_6H_5)_4$–$AlBr_3$ catalyst contains only a single site (for ethylene–propylene copolymers $r_1 = 16$, $r_2 \sim 0.1$)[9,10], so this system was used as a model to test the applicability of the theoretical treatments to the organometallic mixed catalysts.

Experimental

Materials.—Reagent grade cyclohexane was treated with hot sulfuric acid, washed with water, dried with magnesium sulfate and distilled over sodium. Just prior to use, this solvent was redistilled over calcium hydride into one-liter receivers equipped with stopcocks and fittings to allow handling the container without exposing the solvent to the air. Vanadium tetrachloride was obtained from the Union Carbide Metals Company and was handled as a dilute solution in cyclohexane. Tetraphenyl tin was recrystallized from xylene and dried, at 75°, 20 mm., before use. Aluminum bromide was prepared by the direct bromination of aluminum and distilled over aluminum wire. The ethylene was obtained from Union Carbide Olefins Company and contained <30 p.p.m. oxygen, 0.5% methane and 3% ethane. It was passed through an Ascarite and a Linde Molecular Sieve column before use. Propylene, containing about 1% propane, was obtained from Matheson Coleman and Bell and was dried by passage-through molecular sieves.

Polymerization Procedure.—A 3-liter round-bottom flask was fitted with (1) a reflux condenser, (2) a thermocouple well, (3) a stoppered, 30-ml. separatory funnel for introducing catalyst, (4) a gas inlet tube, (5) a fitting to receive the one-liter solvent receiver and (6) a completely sealed magnetic stirrer. The entire apparatus was suspended in an oil bath held at 65 ± 0.1°, charged with tetraphenyl tin, 2.14 g. (5 mmoles), fitted with the solvent container and the catalyst-containing funnel (VCl_4, 0.025 mmole, and $AlBr_3$, 10 mmoles, in 10 ml. of cyclohexane) which had been charged in a drybox. The vessel was purged with dry nitrogen for 1 hr., the cyclohexane solvent then was added and the nitrogen purge continued an additional hour at 1 l./min. The nitrogen flow then was replaced by the ethylene–propylene mixture at atmospheric pressure (14 mole % propylene which corresponds to 40 mole % propylene in the cyclohexane[10]). After purging an additional 30 min. at 1 l./min., the $AlBr_3$–VCl_4 mixture was added dropwise. After 2 to 3 min., pure oxygen (Linde) was metered into the comonomer stream at a constant rate (~0.015%). Upon addition of oxygen, polymerization started and continued at a steady rate. After 45 min., the reaction was quenched by the addition of 2 l. of methanol containing 5 ml. of concentrated hydrochloric acid, the precipitated polymer was removed by filtration, heated at reflux with two separate portions of methanol, removed by filtration and dried giving 7.6 g. of copolymer having an average propylene content of 10.0 mole %. The filtrate from the polymerization was washed with 0.1 *M* hydrochloric acid to remove the catalyst and evaporated to dryness. An infrared analysis of the residue showed no polypropylene oil. The 3.8 mole % propylene copolymer was prepared with a 8.1 mole % propylene feed (27 mole % in cyclohexane).

Under the above conditions only about 10–15% of the monomer that passes through the reactor is polymerized, so there is always a substantial excess of monomer to maintain a saturated solution. Polymerizations can be conveniently carried out for long periods and higher yields (over 100 grams per gram of catalyst). The $TiCl_4$–$(C_2H_5)_3$-Al copolymer was prepared with a ratio of Al/Ti = 5.

Solvent Extractions.—The powdered polymer samples were successively extracted in vapor-jacketed Soxhlet extractors with boiling diethyl ether, *n*-hexane and *n*-heptane, each for 24 hr. The polymer was recovered from each solvent by concentration, precipitation into methanol and drying at 70° under vacuum. The solvent extractions produced no appreciable change in the intrinsic viscosity and propylene content of the uniform copolymers, indicating no degradation during extraction.

Fractionation.—The elution fractionation column was essentially the same as that of Francis, Cooke and Elliott[11] with upward elution. Two grams of the 10.0 mole % copolymer was dissolved in 225 ml. of xylene–cellosolve (3:1) and cooled slowly from 75 to 65° in the presence of 800 g. of sand. This mixture was placed on the top of the column and the fractionation carried out with upward elution at 100° with mixtures of cellosolve and xylene, containing 0.1% N-phenyl-2-naphthylamine. The eluent composition was varied in 20 increments (300 ml., 1 hr. per increment) from 33 to 60 weight % xylene, affording 13 fractions. A final small fraction, taken in tetralin at 150° after an additional 8 hr. to ensure complete removal of polymer, exhibited some apparent degradation. The cumulative weight per cent. values, *W*, were calculated according to $W = \sum_{j=0}^{i-1} w_j + 1/2\, w_i$, where w_i is the weight per cent. of each fraction.

Intrinsic Viscosity.—The specific viscosities, η_{sp}, were measured at a single concentration (from 0.05 to 2 g./100 ml.) in tetralin containing 0.05% N-phenyl-2-naphthylamine at 125°. A Ubbelohde viscometer was used, with kinetic energy corrections. The intrinsic viscosity, $[\eta]$, was calculated from[12] $c/\eta_{sp} = 1/[\eta] - k_r'c$, where c is the concentration of polymer in g./100 ml. The value of k_r', 0.300, previously determined[13] to be constant for linear polyethylene up to intrinsic viscosities of 11 and shear gradients of 1000 sec.$^{-1}$, was used as a reasonable approximation for the ethylene–propylene copolymers. The molecular weights were estimated from the usual Mark–Houwink equation, $[\eta] = KM^{\alpha}$, with the following constants estimated[14] for a 10 mole % propylene copolymer, $\alpha = 0.74$, $K = 3.94 \times 10^{-4}$, and for the 2.6 and 3.8 mole % copolymers, $\alpha = 0.74$, $K = 4.24 \times 10^{-4}$. With the small samples obtained from the fractionation, the intrinsic viscosity was measured on solutions obtained by dissolving the films after the infrared analysis. The molecular weight calculated from the viscosities of the unfractionated polymers were designated M_v, and the fractions, M.

Infrared Analysis.—The copolymer analyses were conducted by infrared measurements on thin films using a Perkin–Elmer Model 21 spectrometer, with sodium chloride optics, and slit program 9.60. The propylene content was determined at 7.25 microns (1379 cm.$^{-1}$) after compensation[15] of the interfering 7.31 and 7.39 micron bands with a high molecular weight linear polyethylene.[16] The band at

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[3] G. Natta, G. Mazzanti, A. Valvassori and G. Pajaro, *Chim. e ind.* (*Milan*), **39**, 733 (1957).

[4] G. Mazzanti, A. Valvassori and G. Pajaro, *ibid.*, **39**, 743 (1957).

[5] G. Mazzanti, A. Valvassori and G. Pajaro, *ibid.*, **39**, 825 (1957).

[6] G. Natta, A. Mazzanti, G. Valvassori and G. Sartori, *ibid.*, **40**, 717 (1958).

[7] G. Natta, G. Valvassori, A. Mazzanti and G. Sartori, *ibid.*, **40**, 896 (1958).

[8] H. Wesslau, *Makromol. Chem.*, **26**, 102 (1958).

[9] (a) W. L. Carrick, R. W. Kluiber, E. F. Bonner, L. H. Wartman, F. M. Rugg and J. J. Smith, *J. Am. Chem. Soc.*, **82**, 3883 (1960). (b) C. G. Overberger and F. Ang, *ibid.*, **82**, 929 (1960).

[10] F. J. Karol and W. L. Carrick, *ibid.*, **83**, 2654 (1961).

[11] P. S. Francis, R. C. Cooke and J. H. Elliott, *J. Polymer Sci.*, **31**, 453 (1958).

[12] (a) G. V. Schulz and F. Blaschke, *J. prakt. Chem.*, **158**, 130 (1941). (b) W. Heller, *J. Colloid Sci.*, **9**, 547 (1954).

[13] G. E. Myers, private communications.

[14] G. Moraglio, *Chim. ind.* (*Milan*), **41**, 984 (1959).

[15] A. H. Willbourn, *J. Polymer Sci.*, **34**, 569 (1959).

[16] G. W. Phillips and W. L. Carrick, *ibid.*, in press.

TABLE I

PHYSICAL PROPERTIES OF POLYETHYLENE AND ETHYLENE-PROPYLENE COPOLYMERS FRACTIONATED BY SUCCESSIVE SOLVENT EXTRACTION

				Ether extract			Hexane extract			Heptane extract			Residue		
Propylene mole %	Catalyst	Density	[η]	%	[η]	Propylene (mole %)	%	[η]	Propylene (mole %)	%	[η]	Propylene (mole %)	%	[η]	Propylene (mole %)
0	VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$	0.972	0.29	0	..	..	0	..	..	0	..	..	100	0.29	..[a]
2.6	VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$	.929	1.79	0	..	..	0	..	..	100	1.79	2.6	0	..	..
3.8	VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$	.920	2.2	0	..	..	0	.	.	100	2.3	3.7	0	..	..
10.0	VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$	.905	0.95	2	n.d.[b]	n.d.	98	0.93	9.9	0	..	..	0	..	..
10.5	$TiCl_4$–$(C_2H_5)_3Al$	.909	1.5	13	0.37	41	15	n.d.	21	50	1.5	7	22	3.1	2.3
34	VCl_4–$(C_6H_{13})_3Al$[5]		4.2	24	2.7	57	61	5.3	28	15	8.6	15	0	..	..

[a] 0.27 weight % methyl. [b] n.d. = not determined.

7.25 microns (1310 cm.$^{-1}$) was used to determine the degree of compensation. The weight per cent. of propylene in the copolymer was calculated by multiplying the observed absorbance per mil by the calibration factor, 70.4. The precision of the propylene content of the copolymer fractions was limited by the error in the measurement of the thickness ± 0.005 mm. (± 10%). The concentration of phenyl end-groups in the copolymers was determined at 14.36 microns (696 cm.$^{-1}$), after compensation of the 13.86 micron band with a high molecular weight $TiCl_4$–i-Bu_3Al polyethylene sample. The weight per cent. phenyl was calculated by multiplying the absorbance per mil by 21.

Gas Chromatography.—The analyses of the comonomers were carried out with a one-meter activated alumina column at 70°, 6 p.s.i.g., 5- or 25-ml. sample volume, in a Perkin-Elmer Model 154 Vapor Fractometer. The areas under the chromatographic peaks were measured by an Instron Engineering Corporation integrator and the conversions to mole percentage values calculated as described previously.[10]

Density.—The copolymer densities were measured by the ASTM D1505–57T gradient column technique.

Results and Discussion

In a previous paper[16] the observation that oxygen is necessary for sustained polymerization with the VX_n–$Sn(C_6H_5)_4$–$AlBr_3$ catalyst was noted, and changes in polymer molecular weight with changing oxygen concentration were described. In this work the oxygen concentration was maintained at a steady, low level to minimize molecular weight fluctuations and to maintain a sufficiently low rate of polymerization to ensure that the diluent is continuously saturated with monomer. Copolymers, containing 2.6, 3.8 and 10.0 mole % propylene were prepared under these conditions. The copolymers were successively extracted with boiling solvents in the series diethyl ether, n-hexane, n-heptane as described by Natta and co-workers.[3] The more highly branched (higher propylene content) copolymers are more soluble than the less branched products, so that the extraction with progressively higher boiling solvents removes the higher propylene content product first and the lower propylene content products last. A linear ethylene homopolymer, even of low molecular weight, is completely insoluble even in the highest boiling solvent, n-heptane (sample 1, Table I).

As shown on Table I, the 2.6 and 3.8 mole % propylene copolymers were completely soluble only in n-heptane, with no residue, indicating a narrow composition distribution and the lack of ethylene homopolymer. The 10.0% copolymer was completely soluble in n-hexane with a small ether-soluble fraction.[16a] These results are contrasted with the broad composition distribution found for a copolymer containing 10.5% propylene, prepared with the heterogeneous, titanium tetrachloride-triethylaluminum catalyst. This sample contained a high propylene fraction which dissolved in ether (13%) and a low propylene fraction which did not dissolve in boiling n-heptane (22%). Natta and co-workers[3,5–7] have also reported extraction results on a variety of copolymers prepared by heterogeneous catalysts, and in every case the composition distribution was very broad as illustrated by sample 6, Table I.

Further information about the homogeneity of the 10.0 mole % propylene copolymer was obtained by an elution fractionation on a sand-trap column above the melting point of the copolymer. Under these conditions, the fractionation results would be influenced by polymer molecular weight and composition distributions but not by the polymer degree of crystallinity. The data characterizing the 14 fractions are shown in Table II. The weighted average intrinsic viscosity of the fractions was within experimental error of the intrinsic viscosity of the unfractionated copolymer. This implies negligible degradation of the copolymer (the last, small fraction experienced an excessively long heat treatment during fractionation). In Fig. 1, the

TABLE II

FRACTIONATION OF AN ETHYLENE–PROPYLENE COPOLYMER

10.0 Mole % VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$ catalyst

Fraction no.	Weight (g.)	Weight % (w_i)	Cumulative weight % W	Propylene (mole %)	[η] (dl./g.)	M
1	0.0503	2.5	1.2	..	*ca.* 0.1	1,800
2	.2227	11.2	8.1	10.9	.26	6,400
3	.1945	9.8	18.6	10.9	.42	12,000
4	.2737	13.8	30.4	11.0	.57	19,000
5	.2827	14.3	44.4	10.1	.75	27,000
6	.1283	6.5	54.8	10.4	.86	32,000
7	.1025	5.2	61.0	9.4	.94	37,000
8	.0982	5.0	65.8	10.2	1.04	43,000
9	.1067	5.4	71.0	9.4	1.14	48,000
10	.0804	4.1	75.7	10.5	1.18	50,000
11	.0876	4.4	80.0	9.4	1.27	55,000
12	.1372	6.9	85.6	10.2	1.48	68,000
13	.1906	9.6	94.0	9.4	1.85	92,000
14	.0265	1.3	99.3	..	1.72	83,000
					0.885[a]	
Unfractionated copolymer				10.0	.884 .870	(M_v) 34,000

[a] Weight-average intrinsic viscosity.

[16a] After completion of the manuscript, a 27 mole % propylene copolymer was prepared by the $AlBr_3$-VX_n-$Sn(C_6H_5)_4$ catalyst and was found to be completely soluble in boiling ether; however, its molecular weight was somewhat lower, η = 0.46.

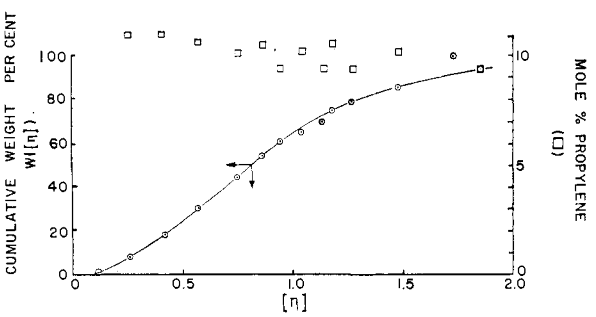

Fig. 1.—Cumulative weight per cent. and mole per cent. propylene for an ethylene–propylene copolymer (VCl_4–$(C_6H_5)_4$ Sn–$AlBr_3$ catalyst, 10.0 mole % propylene).

cumulative weight per cents. and propylene contents of the fractions are plotted against the corresponding values of the intrinsic viscosity. The viscosity values ranged from 0.1 to 1.85 dl./g., and the propylene contents were within ±1.0 mole % propylene of the value for the unfractionated copolymer, 10.0 mole % propylene. The narrow range of compositions is in agreement with the results of the successive solvent extractions above. These results can be compared with the composition distribution predicted from copolymerization statistics by Stockmayer[2] (Fig. 2). Thus, the 10.0 mole % ethylene–propylene copolymer prepared with the soluble catalyst, VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$, appears to be in accord with the random copolymerization statistics.

A sample that was efficiently fractionated on a molecular weight basis (Fig. 1) would likely have been fractionated also with respect to a broad composition distribution, if such were present, since the solvent interaction parameters, χ_1, in tetralin at 135° for example, for polyethylene (−0.259) and polypropylene (0.032) are quite different.[14]

The theoretical composition distribution[2] for the corresponding 2.6 mole % copolymer is also shown in Fig. 2. Copolymer species containing less than 1.5% average propylene are predicted to be in negligible concentration. Since the 2.6 mole % copolymer exhibited no insoluble residue and was completely soluble in heptane, it is reasonable to assert that it, and the 3.8 mole % copolymer, are random copolymers, although complete fractionations were not carried out.

The polymer unit cell dimensions from X-ray diffraction experiments provide additional evidence for the uniformity of these copolymers. Swan[17] has shown that, at a given propylene composition, the uniform copolymers produce a greater expansion of the crystal lattice dimension, *a*, than the non-uniform copolymers. The *a*, *b* and *c* dimensions, respectively, measured[17] on these three copolymers, were: 7.549, 4.968, 2.544 Å. for the 2.6% propylene copolymer; 7.556, 4.967, 2.548 Å. with 3.2% propylene; and 7.755, 4.978, 2.548 Å. with 10% propylene.

The M_w/M_n ratio for the 10.0 mole % copolymer was calculated to be 2.2 on the assumption that the fractions (Table II) were monodisperse (M_w/M_n = 1). Since the molecular weight distribution of the *fractions* is probably somewhat broader than monodisperse, the correct M_w/M_n ratio may be slightly higher than 2.2; however, there can be no doubt that the distribution approximates the "most probable" distribution. A similar, relatively narrow distribution for ethylene homopolymers prepared by this catalyst has been reported previously.[9]

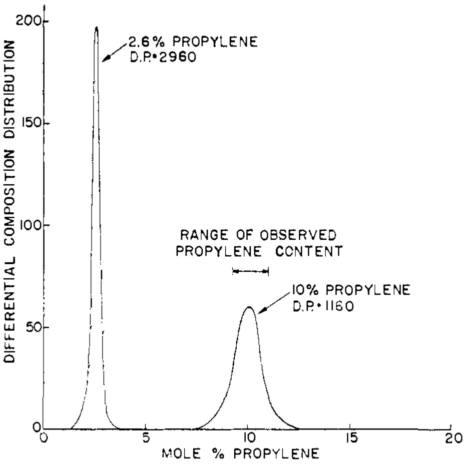

Fig. 2.—Theoretical composition distribution of random ethylene–propylene copolymers.

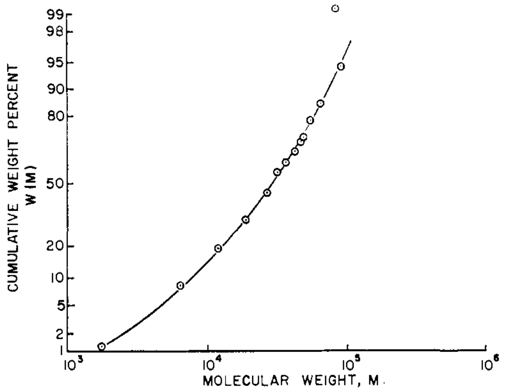

Fig. 3.—Wesslau plot of ethylene–propylene copolymer (VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$ catalyst, 10.0 mole % propylene).

Others have used different techniques for comparing the relative breadth of molecular weight distributions for polyolefins. For example, many low pressure polyolefins, when plotted by the Wesslau[18] method, gave linear plots indicating a very broad molecular weight distribution.[11,19] In contrast, the 10.0 mole % copolymer exhibited a definite upward curvature (Fig. 3) showing the absence of the very high molecular weight tail found in more typical Ziegler-type polyethylenes. Weakley, Williams and Wilson[20] employed the Tung[19] distribution,

$$W(M) = 1 - \exp.\ [-a(M/M_n)^b] \qquad (2)$$

to compare fractionation data with the theoretical distributions. The Tung plot for the 10.0 mole % homogeneous copolymer is shown in Fig. 4. The constants, a = 0.13 and b = 1.3, were estimated at M/M_v = 1.0. The value M_v of 34,000 for the unfractionated copolymer employed in place of M_n

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[17] P. Swan, *J. Polymer Sci.*, in press.

[18] H. Wesslau, *Makromol. Chem.*, **20**, 111 (1956).

[19] L. H. Tung, *J. Polymer Sci.*, **24**, 333 (1957).

[20] T. J. R. Weakley, R. J. P. Williams and J. D. Wilson, *J. Chem. Soc.*, 3963 (1960).

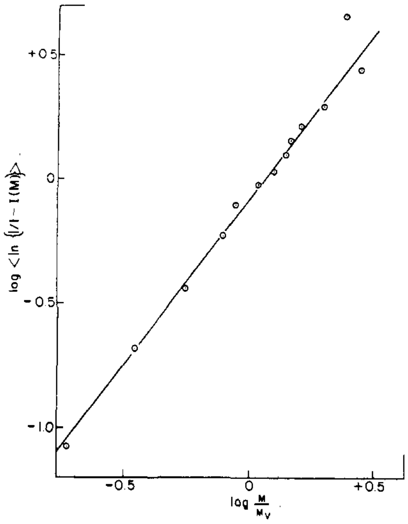

Fig. 4.—Tung plot of ethylene-propylene copolymer (VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$ catalyst, 10.0 mole propylene).

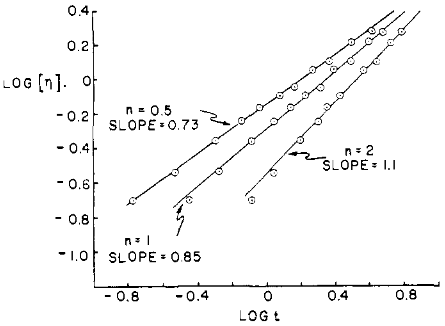

Fig. 5.—Mussa plot of ethylene–propylene copolymer (VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$ catalyst, 10.0 mole % propylene).

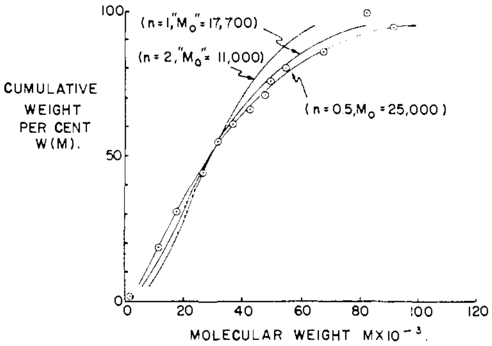

Fig. 6.—Cumulative distribution curve of ethylene–propylene copolymer (VCl_4–$(C_6H_5)_4Sn$–$AlBr_3$ catalyst, 10.0 mole % propylene).

does not alter the slope b. Narrow distribution polymers with M_w/M_n of 1.5 to 2.0 were shown[20] to possess higher slopes, b = 2.1 and 1.6, respectively, at $M/M_v = 1$. On the other hand, fractionation of the broad molecular weight distribution Ziegler polyethylenes prepared with heterogeneous catalysts (M_w/M_n of 14 to 30) exhibited two intersecting lines on the Tung plot with b-values from 0.4 to 1.1.[19]

The treatment of Mussa[21] also provides an estimate of the distribution, insofar as the copolymer can be represented by an exponential distribution equation of the type.

$$W(t) = \frac{1}{n!}\int_0^t t^n e^{-t}\,dt \tag{3}$$

where $W(t)$ is the cumulative weight distribution as a function of the normalized variable $t = M/M_0$, and M is the molecular weight of the fractions calculated from the intrinsic viscosities. The constant M_0, described below, may be related to the number-average degree of polymerization.[21] The parameter, n, characterizes the breadth of the distribution. In this method, experimental values of log $[\eta]$ (Fig. 1) are re-plotted against the theoretical values of log t for the exponential distribution, at equal values of the cumulative distribution, *i.e.*, $W([\eta]) = I\ (t)$. The treatment is carried out for several values of n (as in Fig. 5). Since polyolefins follow the Mark–Houwink equation

$$\log [\eta] = \log K + \alpha \log M \tag{4}$$

a plot of log $[\eta]$ *vs.* log t will be a straight line corresponding to

$$\log [\eta] = \alpha \log t + \log [\eta]_0 \tag{5}$$

in which $[\eta]_0$ is the intrinsic viscosity of a monodisperse sample having a molecular weight M_0. If the experimental fractions were monodisperse, the appropriate value of n in equation 3 is the one which yields a slope of α(0.74 for the ethylene–propylene copolymers[14]) in Fig. 5.

The linearity of the Mussa plot indicates the absence of a broad distribution of chain branches. A slope of 0.74 was found for the exponential distribution with $n = 0.5$. Such a distribution corresponds, upon integration of equation 3, to a ratio of weight-to-number-average molecular weights (M_w/M_n) of 3.33. Thus, the fractions from the 10.0 mole % ethylene–propylene copolymer exhibited, by Mussa's treatment, a molecular weight distribution slightly broader than the "most probable" distribution ($n = 1$, $M_w/M_n = 2$). The distribution is much more narrow than the distributions of most other reported low pressure polyethylene samples which show pronounced sigmoid behavior in the Mussa plot of an exponential distribution.[22] No polymerization mechanism is known to predict an exponential molecular weight distribution with $n = 0.5$. However, small variations in the oxygen concentration could affect the termination reaction, as discussed previously,[16] producing a broader molecular weight distribution without affecting the randomness of the comonomer distribution. The slope of the Mussa plot depends upon the constancy of the M_w/M_n ratio in the fractions. Since the fractions were probably not monodisperse, the log $[\eta]$ of each *fraction* would depend upon *its* molecular weight distribution, and by substituting $(M_w)/M = k$ in equation 4, one obtains

$$\log [\eta] = \log K + \alpha \log (M_w) - \alpha \log k \tag{6}$$

A progressive variation in the breadth of distribution of the fraction so that k changes from 1.1 in the first to 1.5 in the last (highest molecular weight fraction) is sufficient to change the slope of the $n = 1$ curve from the value of 0.74 required by the Mark–Houwink equation to the observed value of 0.85 (Fig. 5).

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(21) C. Mussa I.V., *J. Polymer Sci.*, **26**, 67 (1957).

(22) C. Mussa I.V., *ibid.*, **29**, 171 (1958).

The integral distribution curve for the 10 mole % copolymer is shown on Fig. 6. The value of M_0 for the $n = 0.5$ curve (equation 3) was calculated from the value of $[\eta]_0$ in Fig. 5. The other two theoretical distribution curves were computed from equation 3[21] by selecting values of "M_0" which caused all three curves to coincide at $W(M) = 50\%$. Inspection of the figure again shows that the distribution approximates the most probable distribution, for which case Stockmayer's[2] calculations were made.

In conclusion, it may be stated that the composition distribution of the above copolymers is within the experimental error of that predicted by Stockmayer's statistical analysis, thus demonstrating that polymerizations by the organometallic mixed catalysts are amenable to the same kinetic and statistical treatments that have been applied to the classical catalysts. The uniformity of the copolymers prepared by the soluble, $AlBr_3$–VX_n–$Sn(C_6H_5)_4$, catalyst strongly supports the view that the heterogeneous copolymers usually prepared by the mixed catalysts are due to a multiplicity of active sites. Obviously, the relative concentrations of the various sites will depend on the specific catalyst formulation techniques employed; therefore, for these mixed catalysts, quantitative comparison of copolymerization kinetic data from different sources will be difficult unless detailed composition distributions are routinely included along with the reactivity ratio values, and care is taken to insure that only one active species is present.[23]

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(23) This work was presented at a Symposium at Polytechnic Institute of Brooklyn, April 29, 1961. At the same Symposium, C. A. Lukach also presented a paper showing a narrow composition distribution in copolymers (approximately 30 mole % propylene) prepared with aluminum alkyl + alkyl vanadate catalysts, and G. Bier, *Angew. Chem.*, **73**, 186 (1961), also has recently reported that vanadium catalysts are more homogeneous than titanium catalysts.

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Reactions between Deuterium and Olefins in the Liquid Phase on Platinum Oxide Catalysts[1]

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The liquid phase deuterogenation of 1-hexene, $\Delta^{1,9}$- and $\Delta^{9,10}$-octalin on platinum oxide catalysts has been investigated at room temperatures in the liquid phase. The deuterogenation of 1-hexene is accompanied by isomerization to *cis*- and *trans*-2-hexene at a rate 3% of that of deuterogenation and by formation of deuteriated hexene of which 90% is 1-hexene at a rate 30% of that of deuterogenation. Most of the saturated product consists of hexane-d_0 to -d_6 with $d_{\text{av.}}$ about 2.0. Similar isotopic distribution appears in the decalins produced from $\Delta^{1,9}$-octalin (54% *cis*-, 46% *trans*-decalin). Exchanged $\Delta^{1,9}$-octalin is formed but no isomerized octalins. These data appear consistent with adsorption of olefin as a *vic*-diadsorbed species, conversion to mono-adsorbed alkane followed by alternation between mono- and diadsorbed alkane. Isotopic exchange between surface H-atoms and gas phase deuterium is slow relative to desorption of monoadsorbed alkane. $\Delta^{9,10}$-Octalin can be hydrogenated only by adding acetic acid or by prereducing the catalyst in dilute acid. In the latter case the product is 61% *cis*- and 39% *trans*-decalin, reaction is slow and d_{av} is nearly 3.0. In all of the *trans*- and 85% of the *cis*-decalin, at least three hydrogen atoms have been equilibrated with the surface H,D-atom pool in contrast to the situation with $\Delta^{1,9}$-octalin where only two hydrogen atoms have been equilibrated in 75% of the product decalins. Most of the *cis*- and all of the *trans*-decalin produced from $\Delta^{9,10}$-octalin appear to be derived from a common intermediate in which three hydrogen atoms are equilibrated, possibly $\Delta^{1,9}$-octalin-10-*d*.

Although our understanding of the mechanistic details of heterogeneous catalytic reactions remains seriously inadequate, substantial advances have been made recently toward a reasonably satisfactory mechanistic interpretation of heterogeneous catalytic reactions between hydrogen and hydrocarbons in the vapor phase. This work constitutes a development and extension of the classical Horiuti–Polanyi mechanism for olefin hydrogenation, and it has come from studies involving isotopic tracers, stereochemistry and variation in hydrocarbon structure rather than from mere kinetics. References to reviews of this work are given in the footnotes.[3–5]

This theory would represent reactions among butylenes, butane and hydrogen as shown in Fig. 1.[6] Catalytic sites on the metallic surface are indicated by asterisks. To simplify the diagram, hydrogen atoms attached to surface sites, *-H, have been omitted. The stereochemistry and geometric arrangement at the carbon atoms bonded to the surface in *vic*-diadsorbed butanes (II, V, VI)[7] appears to resemble that of eclipsed ethanes.[5,7]

Mere hydrogenation of 1-butene occurs by the sequence I, II, III, IV. Isomerization of 1- to *trans*-2-butene, for example, can occur *via* the sequence I, II, III, V, VIII.

In Fig. 1, 2-monoadsorbed butane[7] (III) and 3-monoadsorbed butane (IX) are identical as are the two butanes, IV and X. Substitution of deute-

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(3) T. I. Taylor in "Catalysis," edited by P. H. Emmett, Reinhold Publishing Corporation, Vol. V, New York, N. Y., 1957, Chapt. 5.

(4) C. Kemball, *Advances in Catalysis*, **11**, 223 (1959).

(5) (a) R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957). (b) *Rev. inst. franç. pétrole*, **15**, 145 (1960).

(6) See, for example, G. C. Bond and J. Turkevich, *Trans. Faraday Soc.*, **49**, 281 (1953).

(7) R. L. Burwell, Jr., B. K. C. Shim and H. C. Rowlinson, *J. Am. Chem. Soc.*, **79**, 5142 (1957). A description of the nomenclature of adsorbed species appears on p. 5145.